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CHEMICALS OF COMMERCE

Chemicals of Commerce

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and
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PREFACE

This volume has been prepared to meet a definite need. It is intended as a source of information on the composition of actual commercial products. This is not a chemical dictionary which gives a brief description of all chemical compounds. Many compounds found in such a source are omitted because not widely and readily available. In the case of some materials it may give little more information than would be found in such a source. Others are of sufficient trade importance to justify detailed description. Many products are included such as commercial grades of benzene, or compositions of varied iron oxide pigments, which are to be found only in manufacturers' publications but which are commercially important. Often the only way to get facts concerning such materials has been to obtain directly such information as the producer was willing to disclose. Trade information tends toward expansion of the original and remarkable properties of the product, rather than on its essential composition and method of preparation or manufacture. Knowledge of the latter forms a better foundation for judging what a product will do and why, than do advertising statements.

The price-quotation pages of current trade publications have been used as the principal criterion of what is sold in sufficient quantity to recommend its inclusion. The term chemical is used with a very broad meaning and is intended to cover basic materials; in many cases these are more or less pure chemical compounds, in other cases they are mixtures containing several ingredients.

The book is designed to give in brief concise form the salient facts about any class of materials. Classification is by type of compound, so that closely related substances will occur in the same chapter. This should be of value when it is possible for the user to make a choice among related substances. Where feasible, relative cost is indicated, leading to economy in application. Each chapter starts with a discussion which gives the reader the general background and chemical nature of that particular group of substances. This serves as a brief summary of the usual textbook information and also includes facts relating to the commercial aspect of the products. Because of the need for brevity, it is not an exhaustive text on any one subject but is intended for the practical man, or for the theoretical man looking for practical information. Following the general discussion, the individual products are described. The more important ones are given first. Chemicals falling in more than one group have been assigned to that believed most important. A detailed explanation of the organization of the material is given in the last part of chapter I.

Some technical language has necessarily been used, but the attempt has been made either to define terms, or to limit them to those familiar to one with an elementary knowledge of inorganic and organic chemistry. Equations of reactions have been avoided. Chemical formulas are used in order to define composition and structure briefly.

In addition to other data, experience of the staff of Foster D. Snell, Inc., in working with commercial chemicals, has been included to such a degree as is practicable.

It is hoped that the chemist will find the book useful as a quick source of summarized information about products as a class. We feel that such a summary will serve a useful purpose in our own laboratory. The terminology and presentation have been made as nontechnical as possible in the belief that the book will be useful to the manufacturer and others connected with the chemical industry who may not have advanced technical training. We hope this will not detract from the usefulness of the book to the chemist who wishes to obtain information concerning the numerous commercial materials which are not textbook chemicals.

The material supplied is intended to answer the question so often put to us, "What can I refer to that will give me a brief summary of ———— in commercial terms?"

The blank has been filled in, in numerous conversations, with such subjects as "plastics," "proteins," "pigments," etc. With such a broad scope, there is necessarily the danger of incompleteness. Inaccuracies are bound to creep in, be one ever so careful. Criticisms, suggestions and comments are welcomed.

FOSTER DEE SNELL
CORNELIA T. SNELL

June 1939

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CHAPTER I

INTRODUCTION

A great volume of chemicals is handled by people without formal chemical training. **Grade and quality designations** must be understood in the purchase and use of chemicals, and are accordingly explained in the following paragraphs.

The term **C. P.** stands for **chemically pure.** Materials bearing this label may be supposed to contain a minimum of impurities, but the term is somewhat general and does not mean specifically 100 per cent pure. Strictly speaking, no chemical is absolutely pure although the known impurities may be expressed as present to the extent of 0.0001 per cent. **U.S.P.** is an abbreviation for United States Pharmacopoeia and when applied to chemicals means that they meet the standards given in that publication. Various editions of the Pharmacopoeia may be indicated by such references as U.S.P. X. When the edition is not specified, U.S.P. XI is meant. This is the edition official from June 1, 1936. Many more chemicals are available in C.P. and U.S.P. grades than are referred to in this book. In general, C.P. grades of reagent chemicals are available of all stable materials. Reference to C.P. and U.S.P. grades indicates that such volume is produced as to warrant regular price quotation of that grade. **N.F.** means that the substance meets the requirements described in the National Formulary, published by the American Pharmaceutical Association.

The less pure commercial grades will necessarily be discussed in many cases. Some of the terms used may be applied to only a few substances belonging to a particular type. Some products are commonly produced of a quality so close to pure that grading is unnecessary. Cane sugar is one example, magnesium sulfate another. Others, particularly natural products rather than those manufactured, may in the extreme case contain a major portion of impurity, and only a minor percentage of the material named.

The term **technical** or **technical grade** is applied to products as they are commonly produced on a large scale. The degree of purity of technical products varies with the individual substances and depends on the ease with which contaminants are removed during the manufacturing process. Such relative terms as **crude** and **refined** are also used. A crude grade implies a substance in the form in which it is obtained; for example, a vegetable wax in its natural state as it is collected from the shrubs producing it. Refined substances have undergone treatment to remove at least a part of the original contaminants. Many times there are several grades of the refined product, particularly where the crude product is dark-colored, and the refined light-colored or white. Color itself is in some cases a useful designation. Waxes such as ceresin and beeswax are sold as white and yellow, the former having been bleached to remove the natural color.

Hydrates may be a source of confusion to the nontechnical user. Salts often combine with water chemically to form definite compounds. To illustrate, let us compare soda ash, Na_2CO_3, and washing soda, $Na_2CO_3,10H_2O$. Both are forms of sodium carbonate. The first consists of 100 per cent sodium carbonate, less solid impurities. The second, although a solid, consists of 37.1 per cent of sodium carbonate and 62.9 per cent of **water of hydration.** The term **water of crystallization** is often used for this but water of hydration is preferred because the former implies incorrectly that the water is necessary for the compound to be in crystalline form. For chemical use, washing soda could only compete with soda ash at a price about one-third as great, which practically would never be the case. Salts are sometimes described as anhydrous, containing no water of hydration, and sometimes as crystallized. In the latter case it means that the salt contains the amount of water of hydration which is most common in the trade for that salt. For example, crystallized sodium sulfate or Glauber's salt refers to the decahydrate, $Na_2SO_4,10H_2O$. When the water of hydration is large and variable, $(H_2O)_n$ is used in the formula.

The method of preparation of a substance may be significant. Two grades of manganese resinate are **fused,** and **precipitated.** The former is a poorer grade because it contains whatever impurities were present in the original substances undergoing reaction, while the precipitated form is largely separated from soluble contaminants.

Some compounds are separated from others with which they occur by means of a filter press, or by hydraulic pressure. Stearic acid is separated from liquid oleic acid by the second method. The amount of oleic acid present will be diminished with successive pressings, so that **triple-pressed** stearic acid contains more actual stearic acid than **single-pressed** or **double-pressed** grades.

A material which is reduced to a powder by grinding may be subsequently classified according to the size of the particles. While not always true, such products are normally finer and of a better grade when **wet-ground** than when **dry-ground.** The fineness of a powdered material may be designated by the fineness of a wire sieve through which it will pass, such as a grade of barium carbonate in which 99 per cent will pass through a 200-mesh sieve. Similarly bentonite is prepared having a degree of fineness such that 96 per cent will pass through a 300-mesh sieve. The **mesh** indicates the number of openings to the square inch of the screen used.

Some substances are graded by their content of a particular constituent, or of an active principle. Most fertilizer materials are classed by their percentage content of ammonia nitrogen, phosphate or potash. Commercial tanning extracts are classed by their tannin content.

The **concentration** of liquids is often expressed in terms of **specific gravity,** the weight of a unit volume as compared with that of an equal volume of water. This may be given as such, or by some arbitrary scale such as degrees Baumé. Phosphoric acid may be described as having a concentration of 50 per cent by weight, meaning 50 per cent acid and 50 per cent water, which corresponds to a specific gravity of 1.347, which is about 36.4° Bé. Concentration described in terms of per cent usually means per cent by weight. Alcohol is an exception; the usual concentration of 95 per cent refers to 95 per cent by volume. Alcohol has another designation, that of **proof.** This is based on a proof gallon containing 50 per cent of alcohol by volume. Therefore 95 per cent alcohol is 190 proof; absolute alcohol is 100 per cent alcohol, or 200 proof; 90 per cent alcohol, 180 proof. Another liquid which has its own classification is hydrogen peroxide. This may be described by numerical **volume.** For example, 30 per cent by weight hydrogen peroxide is 100 volume; 3 per cent is 10 volume. This means that a 30 per cent solution gives up 100 times its volume of oxygen gas and a 3 per cent solution gives up 10 times its volume of oxygen gas.

Volatile liquids may be classified by their **distilling range,** such as 30-60° petroleum ether, which boils or distils between 30 and 60° C. Volatile inflammable liquids may have their **flash point** listed, the temperature at which the vapor-air mixture ignites under definitely controlled conditions. The higher the flash point, the less dangerous the liquid is to use, but in general, the more slowly it will evaporate.

Relatively viscous liquids may be described in terms of **viscosity.** This may be expressed in units of absolute viscosity—centipoise, millipoise, etc., as calculated from viscosimeter measurements, or in relative terms, such as the number of seconds required for a ball of standard size and weight to fall through a measured height of the liquid under specified conditions. The viscosity of glue is usually expressed in absolute terms, that of nitrocellulose in relative terms.

Temperatures are given in degrees Centigrade rather than Fahrenheit, unless the latter is the practice in a particular trade. A table inside the front cover will readily permit conversion when the other form is desired.

Cross references to the numerous names of common substances have been avoided. The compound can be located through the index under any of its special names and a multitude of cross references thus avoided. In general, the major classification is by the chemical name with trade terms following. The latter because of their common usage are often employed in discussion. Many obsolete names have been omitted. For identification of such names the reader is referred to any unabridged dictionary, the usual chemical dictionaries, and for medical substances, to Merck's Index.

Solubility is briefly indicated. If less than one part by weight is soluble per 100 parts of solvent, the material is called slightly soluble; if soluble at 1 to 10 parts per 100 parts of solvent, moderately soluble; above that, very soluble. When the solubility approaches or passes one part in one part of solvent it is called extremely soluble. When two liquids can be mixed in all proportions they are referred to as miscible. When referred to only as soluble, data are lacking or are of doubtful quantitative value. When inorganic salts are said to be soluble in organic solvents, the solvents usually refer to alcohol or ether. Figures for solubilities can be obtained from tables in chemical handbooks or other sources if more specific information is necessary. Suitable references are Van Nostrand's Chemical Annual, The Handbook of Chemisty and Physics or, in case more comprehensive data are needed, the International Critical Tables.

Methods cf manufacture are outlined briefly so far as known. In many cases more modern procedures may be in use but such methods are often not disclosed by the manufacturer. Many companies have methods which are strictly their own and which are not known to anyone outside of their personnel. Inclusion of methods of manufacture or of the general type of reaction involved, has three purposes. The first is to permit chemists to estimate probable impurities. A second purpose is to indicate the probable quantity produced. For example, one would not want to plan on using a ton a day of a material which is a by-product of a relatively unimportant industry. The third purpose is to stress to nonchemists the interdependence of different phases of the chemical industry.

Uses are outlined. With rare exceptions any common chemical has a multitude of uses. Only the major ones have been given and the noninclusion of any particular use by no means indicates that it is not an important one. It is intended to list sufficient uses to be suggestive of possible applications. Any attempt to give an inclusive description of the uses of a material becomes too lengthy and too vague. To illustrate, one might give as a use for manganese the flash coloring of brick. Similarly, zinc, and chromite, and salt could be so listed. Then the color or colors obtained with each should be given. Such relatively minor uses do not justify the space required, nor do uses which seem meaningless unless accompanied by a detailed explanation.

Poisonous properties are stressed only where they exist to an extreme degree, such as in cyanides or arsenic compounds. Nearly all chemicals are poisonous, it being a matter purely of degree. For example, sufficient sodium chloride is poisonous although a moderate amount is a necessary element in food. The Caustic Poison Act is summarized in Appendix A.

Hazards in the handling of chemicals are mentioned only in unusual cases. The shipping container necessarily carries much information on this subject. One might say that a man is safer handling a carboy of sulfuric acid than he is driving an automobile, because the carboy is marked "Danger—Handle with Care."

Melting points or **boiling points** are rarely given. It is assumed that a person who uses a book such as this will have available a chemical handbook giving such properties for the pure substance. Since the chemicals of commerce are seldom pure, the exact values for the pure compound would rarely be applicable to the commercial product. Such figures, if they appeared here, might be confusing rather than helpful. This may seem an important omission but has appeared desirable.

Organization of material is by chapters relating to similar products. Thus all sodium salts of inorganic acids are in one chapter, strontium salts are a unit part of another chapter, all petroleum hydrocarbons are in one chapter and synthetic esters in another. Within chapters the organization necessarily varies. Each starts with a general discussion of the products included in that chapter. This covers their chemical nature and the outstanding characteristics of the products as a group. Sometimes a general method of preparation can be given here which applies to all, as in the case of esters. Sometimes special terms are defined, as in the case of "edible oil" and "blown oil" in the chapter on fats and oils.

With inorganic substances the large tonnage materials are those from which others are derived and they therefore appear early in the chapter. Those compounds closely related in structure are together, for example, all other sodium compounds of sulfur accompany sodium sulfate. For organic substances the simple compounds are given initially, then more complex ones. Thus the simplest organic acid, formic, is followed by acetic, propionic, etc. All in the aliphatic class are covered before the aromatic type in every instance. With some materials, notably essential oils and natural plant products, there is no such basis of organization. There similar products are closely associated in the sequence of items. It is believed that this results in similar materials being close to each other in each chapter, which is the fundamental idea throughout.

Under each product the sequence is in general: (1) Name, (2) formula, (3) general description, (4) method of manufacture unless a general method is included in the introduction to that chapter, (5) occasional information about common impurities or contaminants when available, (6) commercial grades, and (7) uses. This is not necessarily strictly followed but the order serves to facilitate quick inspection of data.

The **basis of inclusion** of a chemical is its price quotation in recognized trade journals. Those checked are Oil, Paint and Drug Reporter; Chemical Industries; Industrial and Engineering Chemistry; Chemical and Metallurgical Engineering; The Spice Mill; Soap; India Rubber World; and several others. Occasionally a material has been included because of its close relation to another one quoted.

CHAPTER II

INORGANIC ACIDS

An acid is commonly defined as a compound whose positive radical is hydrogen and which gives hydrogen ion when dissolved in water. Acids giving a high concentration of hydrogen ion or high hydrogen-ion activity, such as hydrochloric, sulfuric and nitric acids, are called strong acids. Such acids turn blue litmus red, have a sour taste in dilute solution and are corrosive to metals such as iron. Others which are still true acids exhibit such a low hydrogen-ion activity as to be very unreactive and may even fail to turn blue litmus red in dilute solution. Boric or boracic acid is an example of a very weak inorganic acid.

There are also inorganic acids which are insoluble in water and therefore cannot show the reactions of acids in solution. Tungstic acid is an example of this. They are classified as acids because they combine with bases to form salts.

The subject of inorganic acids is further confused by the industrial application of the term to anhydrides. Such an **anhydride** is defined as the oxide of the element which, when dissolved in water, will form the acid. A typical example is arsenious acid. Structurally this is As_2O_3, the anhydride of arsenious acid, H_3AsO_3. When dissolved in water the anhydride becomes a weak acid because it reacts with the water. When commercially classified as acids, such compounds are described as anhydrides, the commercial form in which they occur. It must be borne in mind that the pure acids may be gaseous, liquid or solid and that they are often available only in aqueous solution rather than in pure form.

In general, acids are neutralized by bases to form salts. In the case of weaker acids this direct reaction is not always possible although the salts may be produced by indirect means. Often acids will react with salts of weaker acids to form a salt of the stronger acid and liberate the weaker acid. Hydrogen is displaced from the stronger acids by the action of strongly electropositive metals such as zinc or iron. From this it will appear that there are various strengths of acids, even differing types, and that some may not even show the usual chemical reactions of acids. Unfortunately the matter is as complex as indicated. The uses of the acids often overlap with uses of their salts and this is a further source of conflict in classification.

Many acids form partially neutralized compounds which are both acids and salts. Such salts will be considered under that class rather than as acids. For example, the classification of the compound having the formula $NaHSO_4$, is "sodium acid sulfate," not "acid sodium sulfate."

Sulfuric acid or **oil of vitriol**, H_2SO_4, is a heavy colorless liquid when pure. Commercial forms may be brown due to the presence of impurities, or turbid due to suspended lead sulfate from manufacture or storage in lead containers. Sulfuric acid reacts with water very readily to form several hydrates. So much heat is given off that great care must be taken in mixing these two liquids. The usual procedure is to add the acid slowly to the water with constant stirring. Because of this affinity for water, sulfuric acid is used widely as a drying and dehydrating agent. Hot concentrated acid is a weak oxidizing agent, and finds some use for that purpose.

Sulfuric acid is relatively nonvolatile and is used to liberate more volatile acids from their compounds. As an acid, it is dibasic and forms both normal and acid salts, such as Na_2SO_4 and $NaHSO_4$. It is a moderately strong acid, although not as strong as hydrochloric and nitric acids. On heating, the acid largely volatilizes as such, but some decomposition into water and the anhydride, sulfur trioxide, occurs.

The chamber process of manufacture, while old, is still the cheapest method of manufacture of the usual technical grades. Sulfur dioxide is produced by burning pyrites or elementary sulfur. Waste gases high in sulfur dioxide from copper and zinc smelters, may be purified and used. Sulfur dioxide, air, steam and an oxide of nitrogen are conducted into lead-lined chambers. The first reaction is to form nitrosyl sulfuric acid. This reacts with the steam present to form sulfuric acid. The oxide of nitrogen is reduced in the process but is reoxidized by air and used over again, with replacement of that lost. A modification eliminates the lead chambers, and the entire process is carried out in a series of acid-proof towers packed roughly with acid-proof brick or flints, to give a large surface for reacting liquids and gases. Chamber acid ordinarily has a concentration of 66 to 80 per cent. It was formerly concentrated by heat to over 90 per cent, but this high concentration is now largely made by the newer contact process.

In the contact process for the manufacture of sulfuric acid, sulfur dioxide is catalytically oxidized with excess oxygen or air to sulfur trioxide, the anhydride of sulfuric acid. This reaction is carried out at an optimum temperature of 425-450° C. Suitable catalysts are vanadium oxide, selenium or platinum dispersed on suitable bases. Since catalysts are easily poisoned and lose their efficiency in the presence of impurities such as arsenious oxide, the burner gas must be highly purified. The sulfur trioxide vapors are led into 98 per cent sulfuric acid, since they would be absorbed only very inefficiently in water. More water is constantly added in order to keep the concentration of acid at this level. This process has the advantages of producing a purer acid than the chamber process, and one which can be adjusted to any concentration by adding water or absorbing more sulfur trioxide.

Sulfuric acid is the cheapest liquid acid. For many purposes the presence of reasonable amounts of impurities is not a serious handicap. Its industrial use is so general that the relative demand for it can be taken as an indicator of trade conditions. The volume manufactured is such that it is even transmitted by pipe line for short distances. Some of its uses are in the manufacture of other chemicals such as sulfates and more volatile acids, for the sulfonation of organic compounds, for pickling iron and steel, in electroplating, in metallurgy, in rayon manufacture, in the textile industry, for wax purification, in the manufacture of fatty acids, to neutralize alkalies, as a dehydrating agent, for parchmentizing paper, in engraving and lithography, in storage batteries, in petroleum refining, and in the manufacture of fertilizers, explosives, etc. Its sale is subject to the Caustic Poison Act given in Appendix A.

The C.P. and U.S.P. grades of sulfuric acid usually contain over 94 per cent of acid. It is sold by its density or specific gravity of 1.84 and is often referred to as a 98 per cent grade but seldom reaches that concentration. It is commonly called concentrated sulfuric acid.

Technical grades are sold either by degrees Baumé or percentage of acid. The usual grades are given below in degrees Baumé with the corresponding specific gravity, percentage of anhydrous acid and the factor for calculation of the price per pound. To use this factor multiply the quotation per pound for that grade, by the factor.

Bé	Sp.G.	Percentage of Anhydrous Acid	Factor to Calculate Cost for Anhydrous Acid
60°	1.7059	77.67	1.29
66°	1.8354	93.19	1.075
66.35°	1.8437	98	1.032

Price comparisons should be based on anhydrous acid when purity, concentration and similar factors are not of first importance. Anhydrous acid is the active material paid for. Other concentrations also appear in commerce. The old term "oil of vitriol" generally refers to the 66° Bé grade. The most common impurities are iron, arsenic and lead, and these are substantially absent in acid made by the contact process.

Battery acid is a grade of sulfuric acid especially purified and quoted for use in lead-plate storage batteries. It is sold in varying concentrations from sp. g. 1.2 to 1.835 but quoted on the basis of the concentrated grade. It is colorless and practically free from iron and other impurities.

Fuming sulfuric acid or **oleum** is produced by the contact process described under sulfuric acid. It is in effect a commercial form of the anhydride, sulfur trioxide, SO_3, dissolved in sulfuric acid. The sulfur trioxide is absorbed in sulfuric acid without adding water to keep down the concentration. It reacts with the sulfuric acid to form a compound $H_2S_2O_7$. Commercial grades contain 20 per cent and 65 per cent of excess sulfur trioxide. Its use is largely as a sulfonating agent in the production of organic compounds.

Chlorosulfonic acid, SO_2ClOH, is a colorless to brown fuming liquid of an oily consistency, decomposed by water or alcohol.

It is made by passing hydrogen chloride into fuming sulfuric acid, or by combining sulfur trioxide and hydrochloric acid. A technical grade is sold commercially. It is highy corrosive and because of its fuming nature is readily identified, having many of the characteristics of fuming sulfuric acid. It is used in the manufacture of organic sulfonic chlorides; for example, in the first step in the manufacture of saccharin, toluene is led into an excess of chlorosulfonic acid, which gives a mixture of liquid toluene-*o*-sulfonic chloride and solid toluene-*p*-sulfonic chloride. Other derivatives are used as dye intermediates. Chlorosulfonic acid has been used in the preparation of poisonous war gases.

Sulfurous acid, H_2SO_3, is seldom an article of commerce but easily prepared as a solution of *sulfur dioxide* in water. It acts as a very weak acid and is mainly used as a reducing agent or bleaching material. Sulfur dioxide, the anhydride, is sold in liquid form in pressure cylinders and released by a suitable reducing valve.

Hydrochloric acid, muriatic acid, or **chlorohydric acid,** HCl, is an aqueous solution of the colorless gas hydrogen chloride. The solution fumes unless very dilute. The gas is also soluble in alcohol or ether. The term muriatic acid is commonly used commercially. An ancient name occasionally encountered is **spirits of salt.** As an acid, it is one of the strongest known, nitric acid being about equal to it in strength, and sulfuric acid somewhat less strong. It attacks the skin after brief exposure. Hydrochloric acid was formerly produced principally by the action of concentrated sulfuric acid on common salt. Hydrogen chloride is evolved and absorbed in water. The process was carried out in large iron pans, with the exclusion of air as far as possible from the gas produced. It is a by-product in direct chlorination of benzene or any other saturated organic hydrocarbon. The purest quality is produced by burning hydrogen in an atmosphere of chlorine or combining hydrogen and chlorine in the presence of a catalyst. The common impurities in the cheaper grades are iron, sulfuric acid and arsenic.

The C.P. and U.S.P. grades are a constant-boiling mixture with water, having a specific gravity of 1.19 and containing about 37 per cent of acid. Its volatile nature gives the acid a sharp odor. Commercial grades are usually expressed in degrees Baumé and are given below with the corresponding specific gravity, percentage of anhydrous acid and the factor for calculation of the price per pound of anhydrous acid. To use this, multiply the quotation per pound for that grade, by the factor.

Bé	Sp.G.	Percentage of Anhydrous Acid	Factor to Calculate Cost of Anhydrous Acid
18°	1.1417	27.92	3.58
20°	1.1600	31.45	3.18
22°	1.1789	35.21	2.84
23° or C.P.	1.1885	37.14	2.70

As an inexpensive and strong acid, hydrochloric acid is used for almost any of the purposes where a nonoxidizing acid is desired. Sulfuric acid is cheaper on a per pound basis and on a basis of acid units. As an active acid hydrochloric acid dissolves metallic oxides readily and therefore is used in metal cleaning. Its sale is subject to the Caustic Poison Act, given in Appendix A.

Hydrochloric and nitric acids are sometimes mixed, usually in the proportion of three to one, to form **aqua regia.** The two acids react to form some free chlorine and oxides of nitrogen. Because of the products of reaction it is a powerful oxidizing agent and will dissolve gold and platinum, although neither acid alone will dissolve these metals. This is of more importance in the laboratory than in industry.

Hydrofluoric acid, HF, is an aqueous solution of the gas **hydrogen fluoride.** The gas itself is readily condensed to a liquid boiling at 19.4° C., but is sold as the aqueous solution rather than as the anhydrous liquid. It is corrosive in contact with the skin, and the solution fumes unless dilute. Its chief importance relates to its reaction with silica or sand, and with silicates, when it produces a gas, silicon tetrafluoride, SiF_4. Because of this reaction with silicates, it attacks glass and must be stored in paraffin-coated bottles, in lead, or in rubber containers. The aqueous solution is produced by treating powdered calcium fluoride with concentrated sulfuric acid, distilling the mixture in a retort of platinum or lead, and absorbing the gas in water. In addition to a C.P. grade containing about 48 per cent of acid there are technical grades containing 30, 48, 52 and 60 per cent of the acid, marketed in lead carboys.

Hydrofluoric acid is used in the manufacture of fluorides and other chemicals and as an analytical reagent. In the manufacture of analytical-grade filter paper it is used to remove the silica. Other uses are for removing sand particles from metallic castings, and for etching glassware, such as marking calibrations on chemical glassware.

Hydrofluosilicic acid, silicofluoric acid, hydrosilicofluoric acid, hydrofluosilicic acid or **sand acid,** H_2SiF_6, is a corrosive, colorless, fuming liquid which attacks the skin. It is made by heating sand with powdered calcium fluoride and sulfuric acid in excess, distilling, and absorbing the gas in water. Another source is from gases produced in phosphate manufacture. A 30-35 per cent grade is sold. It is used mainly for production of its salts, which have varied uses.

Hydrobromic acid, HBr, is a colorless aqueous solution of the gas, **hydrogen bromide,** which is also soluble in alcohol. The solutions fume except in dilute solution. It is an active reducing agent but not as active as hydriodic acid. It is quite corrosive to the skin. Hydrobromic acid is manufactured by passing a mixture of hydrogen and bromine vapor over a heated platinum catalyst, and absorbing the gas produced in water. The C.P. grade contains 48 per cent of acid and the U.S.P. grade 10 per cent. The latter refers to standards of U.S.P. VIII. A commercial grade contains 34 per cent of acid. It is relatively expensive. Uses are limited to synthetic organic chemistry for production of organic bromides, as a reducing agent, and for the production of inorganic bromides.

Hydroiodic or **hydriodic acid,** HI, is an aqueous solution of **hydrogen iodide.** This is a gas at ordinary temperatures, extremely soluble in water and soluble in alcohol. The aqueous solution is colorless to pale yellow and fumes in the air unless very dilute. It is a very active reducing agent, being readily oxidized to free iodine. Atmospheric oxygen will oxidize the solution slowly, so that if exposed to the air, hydriodic acid gradually becomes brown due to the presence of free iodine. The gas is produced by mixing red phosphorus and iodine and adding a minimum amount of water slowly. To prepare the solution, powdered iodine is suspended in water and hydrogen sulfide gas introduced. In this process the iodine dissolves slowly in the water and is reduced to hydriodic acid, while hydrogen sulfide is oxidized to free sulfur. The latter is separated by filtration. Another method of preparation is by passing a mixture of hydrogen and iodine vapor over a heated platinum catalyst and absorbing the product in water.

Because of its instability it is not obtainable in a C.P. grade. Commercial grades contain 47 per cent and 57 per cent of the acid. A U.S.P. grade contains 9.5-10.5 per cent of the acid and 0.6-1.0 per cent of hypophosphorous acid. The latter is obtained by distillation to give a constant-boiling liquid. The use of the material is limited because it is relatively expensive. Uses are for the preparation of inorganic and organic iodides, as a reducing agent, as a disinfectant, and in pharmaceuticals.

Hydrocyanic acid, or **prussic acid,** HCN, is an aqueous solution of the gas **hydrogen cyanide.** The gas is very soluble in alcohol or ether. The solution is an extremely weak acid, being displaced by carbonic acid, which is stronger. Both the solution and the gas are highly poisonous. The acid is produced by distilling a concentrated solution of potassium or sodium cyanide with dilute sulfuric acid and absorbing the vapors in water. The so-called U.S.P. grade, a 2 per cent solution, is U.S.P. IX. Technical solutions containing 5 per cent and 10 per cent of acid are sold. The gas, compressed into cylinders, is also marketed. The solutions find use mainly in organic synthesis. The gas is in widespread use as a fumigant in spite of the danger of its poisoning humans. In many ways hydrocyanic acid is closely related to the halogen acids but its commercial use is strictly limited by its highly poisonous nature.

Nitric acid, aqua fortis, or **azotic acid,** HNO_3, is a colorless liquid which is both a strong acid in aqueous solution and an active oxidizing agent. Commercially the aqueous solution is always used. In concentrated form, it fumes in the air. The yellow color often observed in concentrated nitric acid is due to the presence of the gas nitrogen tetroxide, NO_2 or N_2O_4, which is reddish brown and which results from the decomposition of nitric acid. The anhydride of nitric acid, N_2O_5, is only obtainable in solution in nitric acid as the so-called **fuming nitric acid.** Concentrated nitric acid attacks most metals, reacts with the proteins of the skin to form yellow xanthoproteic acids and is extremely corrosive in contact with the skin.

The oldest commercial method of production is by the distillation of a mixture of Chile saltpeter, $NaNO_3$, with an excess of concentrated sulfuric acid in horizontal cast-iron stills. The vapors are condensed in a series of stoneware receptacles. This method tends to include all of the volatile impurities of the saltpeter in the acid. Salt cake or sodium bisulfate is a by-product. A more modern process is by the catalytic oxidation of ammonia, which is mixed with air or oxygen and passed over a catalyst, usually of platinum, at an elevated temperature. The ammonia is oxidized first to a lower oxide of nitrogen, which in turn reacts with the excess oxygen present to form higher oxides, which are absorbed in water to yield dilute nitric acid. The product is purer than in the first process but has to be concentrated after manufacture. Still another method is by the direct oxidation of nitrogen in the atmosphere, called **nitrogen fixation.** An arc discharge between carbon rods is spread out by means of electromagnets and air passed through. About 1 per cent of nitric oxide, NO, is formed. On cooling, this unites with oxygen and the higher oxide is absorbed in water to give nitric acid.

The C.P. grade contains about 70 per cent of nitric acid and has a specific gravity of about 1.42. This grade is also U.S.P. Commercial grades are sold by Baumé readings. The various grades are given below with their corresponding specific gravities, content of actual nitric acid, and a factor for multiplication of the price per pound to permit calculation in terms of anhydrous acid. Yellow nitric acid of a given grade sells for slightly less than colorless acid of the same concentration.

Bé	Sp.G.	Percentage of Anhydrous Nitric Acid	Factor to Calculate Price to That for Anhydrous Acid
36°	1.3303	52.30	1.92
38°	1.3551	56.52	1.77
40°	1.3810	61.38	1.63
42°	1.4078	67.18	1.49
42.75°	1.4181	69.52	1.44

Nitric acid is the cheap oxidizing acid, if we except some applications in which sulfuric acid serves as an oxidizing agent. Its uses are multitudinous. The oxides derived from it form nitrosylsulfuric acid, which is the catalyst in the chamber process of manufacture of sulfuric acid. It is used in the production of organic nitro compounds, as well as many inorganic nitrates. With sulfuric acid it is used in making nitrocellulose, which is the basis of celluloid and lacquer manufacture, and in making the higher nitrated product, gun-cotton, used in the manufacture of explosives. Since it attacks nearly all metals except aluminum it is used for etching and photoengraving. Its sale is subject to the Caustic Poison Act, given in Appendix A.

Phosphoric acid or **orthophosphoric acid,** H_3PO_4, is a colorless liquid. It is tribasic but dissociates principally into the ions H^+ and $H_2PO_4^-$. Dissociation of the $H_2PO_4^-$ ion into H^+ and $HPO_4^=$ is relatively slight. The ion $HPO_4^=$ is hardly dissociated at all. This may be explained in other terms by saying that the monosodium salt is only slightly acid, the disodium salt slightly basic and the trisodium salt strongly basic, these reactions being in each case due to hydrolysis. As an acid it is considerably weaker than hydrochloric and sulfuric acids but it is much stronger than such weak acids as acetic and boric.

The anhydride, **phosphorus pentoxide,** P_2O_5, is a white solid. It absorbs water readily to form phosphoric acid but is not used as such for making the acid. Its main function is as a strong dehydrating agent.

A technical grade of phosphoric acid is made by mixing phosphate rock, which is high in calcium phosphate, with sulfuric acid, heating with steam and stirring. Calcium sulfate is precipitated and filtered off. The filtrate is high in phosphoric acid. Pure phosphoric acid may be made by boiling red phosphorus with slightly diluted nitric acid and evaporating off water and excess nitric acid. The process which is probably most important in the manufacture of the acid is more complicated in operation. Phosphate rock is smelted with coke to give vapors of phosphorus. In contact with air these are oxidized to the anhydride, phosphorus pentoxide, which is not separated as such. Instead, the vapors containing anhydride are mixed with steam and the resulting phosphoric acid condensed in suitable corrosion-resistant tubes, usually made of carbon. Since this gives an acid substantially free from all non-volatile impurities, competitive conditions have resulted in the development of methods of purification of the acid from the older process by volatilization.

The usual C.P. grade contains 85 per cent of phosphoric acid and is syrupy in consistency. U.S.P. grades are sold at 10, 50 and 85 per cent concentrations, of which the 50 per cent grade is U.S.P. X. Technical grades are 50 and 75 per cent concentrations.

The major uses of phosphoric acid are in the form of its salts. The acid is used to make various phosphates, as a substitute for organic acids in foods and soft drinks—in engraving and in lithography. The mono substituted salts are also used for many of these purposes and as the acid ingredient in baking powder.

Hypophosphorous acid, H_3PO_2, is a white crystalline solid which melts at 26.5° C. It is used in aqueous solution and is a powerful reducing agent. It is produced by heating an alkali, usually concentrated baryta water, with white phosphorus, and decomposing the resulting barium salt with sulfuric acid. A 30-32 per cent U.S.P. grade is sold. Its use is a strong reducing agent.

Mixed acid is a commercial product which is a mixture of sulfuric and nitric acids. Various proportions may be obtained according to the requirements of the purchaser, so that it is quoted as so much per nitric unit and so much per sulfuric unit. Standard mixed acid contains 36 per cent of concentrated nitric and 61 per cent of concentrated sulfuric acid. Mixed acid is used for nitrating purposes such as in producing nitrated cotton. The presence of sulfuric acid increases the efficiency of nitration by absorbing the water which is a product of the nitration reaction.

Arsenic acid or **orthoarsenic acid,** H_3AsO_4, crystallizes as a hydrated deliquescent white solid, $2H_3AsO_4.H_2O$, soluble in water and alkalies. It is produced commercially from white arsenic, which is As_2O_3, the anhydride of arsenious acid, by digestion with oxidizing agents. The oxidizing agent used is usually 12 parts of nitric acid and 1 part of hydrochloric acid. The anhydride of arsenic acid, As_2O_5, does not occur as an article of commerce. The acid is sold in varying grades of purity, a 75 per cent grade being a common one. It is used in the manufacture of arsenates, glass and insecticides, and in the textile industry as an assist in printing. All water- and acid-soluble compounds of arsenic are poisonous, including this one.

Arsenious acid, arsenic trioxide, arsenious oxide, arsenious anhydride, or **white arsenic,** As_2O_3, is an anhydride which, dissolved in water, reacts as H_3AsO_3. It is only slightly soluble in cold water but more soluble in hot water, alkalies, alkaline carbonates, alcohol and some dilute acids. It occurs naturally in mineral form and is also recovered from arsenical pyrites by sublimation. It is largely imported from Japan and the Scandinavian countries. The usual commercial form is as a fine white powder. The U.S.P. grade contains not less than 99.8 per cent of As_2O_3. It is used as a reducing agent as in the manufacture of glass, for the production of arsenic acid, in the production of pigments, and in numerous products for its insecticidal action. It is an inexpensive form of poison, when applicable.

Chromic acid, H_2CrO_4, is handled in the form of **chromic anhydride,** CrO_3, which consists of red, deliquescent, needle-shaped crystals. Chromic acid may be obtained electrolytically, or by the addition of sodium bichromate to concentrated sulfuric acid. The crystals may be seen to precipitate out from "cleaning solution" as prepared by the chemist. An aqueous solution of the anhydride is a solution of chromic acid.

The anhydride is sold as a U.S.P. grade containing not less than 95 per cent of CrO_3, as a C.P. grade, and as a technical grade containing over 99 per cent of CrO_3, sometimes quoted as 99¼ per cent. Because of requirements as to minor impurities in such industries as chromium plating there are also special grades. The acid is destructive of living tissue and must be handled with care. Since it is a strong oxidizing agent it is used for that purpose in organic synthesis. Other uses of the acid are in electric cells, in engraving, and as an astringent and germicide. The acid may be used for the manufacture of chromates. In low concentrations the acid and its salts are used as corrosion inhibitors in aqueous solutions, as in ice-plant brines.

Boric acid, boracic acid or **orthoboric acid,** H_3BO_3, is a white solid, slightly soluble in cold water but readily soluble in hot water.

It is slightly soluble in ether and soluble in alcohol and glycerine. Boric acid is a very feeble acid, weaker than carbonic acid. It occurs naturally in Tuscany, where it is emitted with steam and other vapors from cracks and fissures in the earth. A series of basins is constructed over the vents so as to permit the passage of water through them by gravity. The dilute solution of boric acid obtained is concentrated by evaporation of the water, and in the final stage crystals of the solid separate. Boric acid is also obtained from a mineral called boronatrocalcite by treatment with sulfuric acid, followed by evaporation of the solution and distillation with steam. Another mineral, boracite, is decomposed with hot hydrochloric acid to give boric acid. The C.P. and U.S.P. grades are sold in crystalline or powdered form, the U.S.P. containing not less than 99.5 per cent H_3BO_3. A technical grade containing 99.5 per cent of boric acid is sold in the same forms.

Boric acid is known as an antiseptic, but its antiseptic properties are very limited. It is only slightly soluble in water. Its saturated aqueous solution is useful as an eye-wash because it is nonirritating. It has been used as a food preservative, but this use is now forbidden in many countries, including the United States. Industrial applications are in ceramic glazes, as an addition to cement when a very smooth finish is desired, in laundry starch for glazing purposes, in imitation jewels, in metallurgy, as a welding flux, in fireproofing compositions, pigments, paper glazes, to make imitation hard wood from soft wood, and in cosmetics. The best known grade of chemically resistant glass, Pyrex, is a borosilicate.

Carbonic acid, H_2CO_3, is the aqueous solution of carbon dioxide, CO_2, which is the anhydride of the acid. The anhydride is only slightly soluble in water or alcohol but more soluble in alkalies to form carbonates. The acid is not sold as such and is only referred to here because of its relation to other acids. Gaseous carbon dioxide is a commercial product either in the form of compressed gas in cylinders, or as the solid known as **dry ice.** The latter form is not stable for storage, as it gives off carbon dioxide gas directly without going through a liquid state, until the solid has disappeared. As an acid carbonic acid ionizes slightly to give H^+ and HCO_3^- ions. The latter is scarcely ionized at all. It therefore forms two series of salts of which sodium carbonate and sodium bicarbonate are typical.

Tungstic acid, wolframic acid, or **orthotungstic acid,** H_2WO_4, is a yellow solid sold in powdered form. It is insoluble in water but soluble in hydrofluoric acid and alkalies. For production, it is precipitated from a solution of sodium tungstate by boiling hydrochloric acid. Another method of preparation is by decomposition of an ore containing calcium tungstate, with hydrochloric acid. Calcium chloride goes into solution and tungstic acid and insoluble impurities remain as a sludge. It is purified by dissolving in aqueous ammonia, filtering and decomposing with hydrochloric acid, or by igniting in air to tungstic oxide, WO_3. C.P. and technical grades are sold for use as a mordant in the textile industry, in plastics and for production of tungsten wire by reduction of the oxide.

Vanadic acid is not a commercial substance but the term is used to refer to **vanadium pentoxide,** V_2O_5, the anhydride of the theoretical acid. Vanadium pentoxide exists as yellowish red crystals. It is made by igniting ammonium metavanadate, NH_4VO_3. It is only slightly soluble in water but dissolves in alkalies to form vanadates, and in acids such as sulfuric acid to form the sulfate, $(VO)_2(SO_4)_3$. It is used as a ceramic coloring material, as a catalyst, and as a starting material for making other vanadium salts.

CHAPTER III

BASES OR ALKALIES

Base is a general term for compounds which give hydroxyl ion in aqueous solution. A strong base, one which gives a high concentration of hydroyxl ion, is frequently referred to as an **alkali.** By usage either alkalies or bases are general terms for those substances which neutralize acids.

Strong alkalies are described as **caustic,** because they attack animal matter. They dissolve some forms completely, such as wool and the epidermis of the skin. The term caustic is occasionally used, particularly in medicine, as meaning anything which will attack the skin. In that sense, strong acids are referred to as caustic in their action; this use is the less common. Weak bases give a low concentration of hydroxyl ion and are therefore less active in the properties which distinguish this group of chemicals as a class. Bases react with acids to form salts plus water, the well known process of neutralization. Bases dissolve many acid substances not soluble in water, by reacting to form a soluble salt.

Glass and porcelain are slowly attacked by concentrated solutions of alkalies and even to some extent by dilute solutions. In time therefore, the surface of glass in contact with an alkali becomes roughened or etched. This action is too slow to be used commercially for etching but is important in the storage of alkalies in glass.

Salts of strong bases and weak acids hydrolyze in water to give a strongly alkaline solution. They are not discussed with alkalies or bases but are described under their proper classification as salts. For those of importance see sodium carbonate, sodium phosphate, sodium silicate, sodium bicarbonate and sodium borate. Weak hydroxides of many metals react with acids to produce salts but are not used industrially as alkalies.

In the case of ammonia, a gas, which is not itself a base, reacts with water to form one. Similarly, since calcium oxide and barium oxide react with water to form the hydroxides, the oxides as well as the hydroxides will be considered with the alkalies.

Sodium hydroxide, caustic soda, or **sodium hydrate,** NaOH, is a white deliquescent solid. Its aqueous solution is strongly alkaline. The solubility in water is so great that a solution can be prepared containing over 50 per cent of the alkali. It is also soluble in alcohol, ether and glycerine. In some industries the aqueous solution is called **lye,** or **soda lye.** The household product sold under the name of lye is caustic soda.

Caustic soda is manufactured from other sodium compounds. One method starts with sodium carbonate, Na_2CO_3, soda ash. This is treated in solution with slaked lime. The two react to form caustic soda solution and calcium carbonate. The latter is insoluble and precipitates. Large settling tanks are necessary, as the precipitation of calcium carbonate is slow. The supernatant liquid is drawn off from these tanks and partially evaporated to separate impurities, sodium carbonate being considered an impurity when the product desired is caustic soda. Other common impurities are alumina, iron and silica. This solution may be further concentrated for use as such in the process industries, or all of the water may be driven off and the molten caustic converted to a suitable solid form.

The major method of manufacture is by electrolysis. A saturated solution of common salt passes through an electrolytic cell. When the electric current is on, the sodium ions go to the cathode, where they are reduced to metallic sodium. This immediately reacts with the water to form hydrogen and sodium hydroxide. The hydrogen is collected as a gas, while the sodium hydroxide remains in solution. The chloride ions from the salt migrate to the anode where they lose their charge and form chlorine gas which is collected. Water is driven off from the solution of caustic soda and the white solid product obtained. In this process the main contaminating agent is sodium chloride. A very pure product can be obtained. It is interesting to note that the by-products of this process are hydrogen and chlorine. These may be combined catalytically to form hydrochloric acid and the process has then the net result of converting common salt into the acid and base which would react to produce it. More commonly the chlorine is sold as such. This is of economic importance as showing the close interdependence of caustic-soda and chlorine production. Demand for the two must be closely balanced or warehouse stocks of one or the other begin to build up.

Caustic soda reaches the market in varied forms. Analytical grades appear most commonly as sticks crystallized from alcohol, also as pellets and flakes. Caustic soda takes up both water and carbon dioxide from the air, so must be kept in closed containers or it will deteriorate rapidly. Protection from air is important, as some sodium carbonate is practically always formed. The U.S.P. grade contains not less than 95 per cent of total alkali calculated as sodium hydroxide, of which not more than 3 per cent is sodium carbonate. The fact that sodium carbonate is insoluble in a saturated solution of sodium hydroxide is used in the preparation of solutions free from carbonate. Iron and alumina are also insoluble. Commercial forms are as powder, flake, lump or liquid. The solid caustic has usually been allowed to solidify in a destructible container such as a thin metal drum. Therefore usual practice is to cut away this container when the material is needed for use. Quotations are on a basis of sodium oxide equivalent. The standard grade is 76 per cent Na_2O which corresponds to 98 per cent of caustic soda. A 60 per cent grade is sometimes quoted. The liquid caustic is a concentrated solution sold at a competitive price per unit of caustic soda content because of a differential freight rate. Solutions are sold as 47-49 per cent and 70 per cent grades, and refer to actual sodium hydroxide content. Prices are often quoted on a basis of method of preparation such as "ammonia process" caustic, meaning that it has been produced from sodium carbonate which was in turn produced by the ammonia process—or as "electrolytic."

Caustic soda has an important use in converting cellulose to alkali cellulose, the first step in the production of rayon. An even greater amount is used in the manufacture of soap. Ordinary or hard soap consists of the sodium salt of fatty acids. Mercerized cotton is produced by the controlled action of caustic soda solution on cotton. The surface of the fiber is partially dissolved and reprecipitated to give the glossy finish. The textile industry uses caustic soda in many other ways. It is also used extensively by the paper industry, in oil refining, and as a chemical reagent. The rubber industry, tanning, and numerous other fields utilize it to a lesser degree. It is the strong alkali generally used in industry when a water-soluble alkali is essential. Its sale is subject to the Caustic Poison Act, given in Appendix A.

Potassium hydroxide, caustic potash, or **potassium hydrate,** KOH, is a strong alkali very similar in properties to caustic soda, including caustic action on the skin. The two are interchangeable where the application is merely that of a strong alkali. Caustic potash is more expensive than caustic soda and is therefore used less for general purposes. Also caustic potash is less efficient than caustic soda as a neutralizing agent in a ratio of 1.4 parts of the former to 1.0 of the latter. Caustic potash must be differentiated from caustic soda when the alkali metal enters into the end-product of the reaction, as in the saponification of fat. The potassium salt of fatty acids, called potash soap or soft soap, is very different in its physical properties from sodium soap or hard soap. Like caustic soda, caustic potash readily takes up water and carbon dioxide from the air and must be protected from contact with air.

The methods of manufacture are the same as those for caustic soda, the double decomposition of potassium carbonate with calcium hydroxide and the electrolysis of potassium chloride solution. The usual contaminants are potassium carbonate, potassium chloride and excess water. Caustic potash may also be contaminated with alumina, iron, silica and sulfates.

As with caustic soda, a stick form of C.P. or U.S.P. grade is sold. The U.S.P. grade contains not less than 85 per cent of total alkali, calculated as potassium hydroxide, of which not more than 3.5 per cent is potassium carbonate. Technical grades are flake or solid, at 88-92 per cent of alkali, calculated as potassium hydroxide. Both domestic and imported grades are available. A concentrated solution in water is sold with a content of 45 per cent of caustic potash. Major uses are in the production of soft soaps and lubricants, in engraving and lithography, and for manufacture of potassium compounds. Its sale is subject to the Caustic Poison Act, given in Appendix A.

Ammonia, NH_3, when dissolved in water reacts in part to form **ammonium hydroxide,** or **ammonium hydrate,** NH_4OH.

The three terms are applied loosely to the solution, which is in fact a mixture of ammonium hydroxide and dissolved ammonia gas. The solution is also called **aqua ammonia** or **ammonia water.** In a somewhat modified form, usually containing a small amount of soap, it is sold as **household ammonia.** Ammonium hydroxide is a weak base compared with the foregoing alkalies. It is characterized by its strong, penetrating odor which is that of escaping ammonia gas. Ammonium hydroxide can be completely decomposed and driven from aqueous solution in the form of ammonia by boiling. The solution must be handled with care because of its attack on the skin, although this is less serious than that by caustic soda or caustic potash solution.

Liquid ammonia, as distinguished from the aqueous solution, boils at −33.35° C., giving off anhydrous ammonia gas, which is not only very soluble in water but is also soluble in alcohol or ether. While ammonia is produced by the bacterial decomposition of protein matter, this source is of no commercial importance. Large amounts are formed as by-products of the coke and gas industries, coming into the market usually as impure ammonium sulfate. The salt may be decomposed with slaked lime to liberate ammonia. This source furnishes more than half the world supply of free and combined ammonia. While the aggregate amount from that source is increasing as more by-product recovery processes are put into operation, the relative amount is decreasing.

The main source of ammonia as the gas or liquid, and an important source of ammonium salts, is by synthetic manufacture. Such direct synthesis was the goal of the chemist for many years. This became commercially successful about the time of the World War and increase in its use has been enormous since that time. This is not because the world is using so much more ammonia as such, but because the world supply of nitric acid is now largely furnished by oxidation of ammonia instead of by distillation from Chile nitrates. In the synthetic process nitrogen from air liquefaction or from other sources, and hydrogen from water-gas or producer-gas, are caused to combine directly at increased temperatures and pressures in the presence of a catalyst. The latter is usually iron. The Haber process uses 200 atmospheres' and the Claude process 1000 atmospheres' pressure. The temperature is about 600° C., since much below this, the reaction is very slow and much above it the reverse reaction takes place. The process yields pure ammonia without by-products. The ammonia is separated from unreacted nitrogen and hydrogen by cooling until the ammonia liquefies, or by absorption of the ammonia in water.

Another process, but one which has become unimportant as a source of ammonia, is by forming calcium cyanamide by heating coke and limestone together, and subsequently decomposing the cyanamide with superheated steam under pressure.

While the international economic value of ammonia cannot be discussed in detail, some mention is essential. Because ammonia can be converted into nitric acid and then into explosives, a theory of economic self-sufficiency in fixed-nitrogen production led to a large overexpansion in synthetic-ammonia capacity in the late 1920s. As a result of governmental pressure to support such plants, the methods have been refined to such a degree that, provided suitable equipment is available, ammonia is at present the cheapest neutralizing agent except lime. For this to apply, it must be bought as liquid ammonia, not an aqueous solution, and released through suitable reducing valves so that it can be efficiently absorbed in water and used. The following figures are the cost per pound in 1937, of various alkalies calculated to a basis of sodium hydroxide as a standard. Little relative change is to be expected for some years.

	Relative Cost of Amount Equivalent to 1 Pound of Caustic Soda
Caustic soda	1
Caustic potash	3.25
Ammonia	0.64
Lime	0.17

Ammonia of various grades is sold in liquid form in cylinders. These cylinders include tank cars, which are in effect single large cylinders on wheels. The fertilizer grade is cheapest, that for refrigeration is only slightly higher, but pure grades are much more expensive. As C.P. or U.S.P. aqua ammonia the aqueous solution is sold at 28-29 per cent concentration. The U.S.P. grade contains 9-10 grams of ammonia per 100 cc. of solution but the 28-29 per cent grade is quoted as of U.S.P. quality. The commercial solution is a 26° Bé grade, about sp.g. 0.9, containing 29.4 per cent of ammonia gas. This is handled in carboys, drums, tanks or tankwagons. The cost of the aqueous solution is much higher than that of anhydrous ammonia because of the expense of additional containers and transportation of the water fraction. Its sale is subject to the Caustic Poison Act, given in Appendix A.

Liquid ammonia is largely used as a refrigerant. To a lesser extent it finds use in organic synthesis. The solution, aqua ammonia, has a multitude of uses in the manufacture of resins, rayon, rubber, etc., as well as in the manufacture of ammonium salts.

Nitrogen solution is a trade term for a mixture of 60 parts of ammonium nitrate and 40 parts of 50 per cent aqua ammonia. It is a solution containing the equivalent of 45½ per cent of ammonia, sold at a price per ton in terms of per cent of ammonia. Use is as a base, particularly for neutralizing superphosphate in making fertilizer.

Urea-ammonia liquor is a solution of crude urea in aqueous ammonia containing ammonium carbamate. The ammonia content is such that it is shipped under moderate pressure. A typical composition contains 21 per cent of ammonium carbamate, 37.7 per cent of urea, 13.8 per cent of ammonia and 27.5 per cent of water. Like nitrogen solution, it is used for reaction with superphosphate in the preparation of fertilizers, furnishing the necessary combined nitrogen. The usual grade contains 55 per cent of ammonia in various forms.

Calcium hydroxide, calcium hydrate, slaked lime, or **hydrated lime,** $Ca(OH)_2$, is a dry white powder whose solution, called **limewater,** gives a weakly alkaline reaction. Unlike the preceding bases, calcium hydroxide is only slightly soluble in water, 0.17 per cent in cold water and only about half that in hot water. In spite of its low solubility, it has a wide use as an alkali in industry because of its low price. The white suspension of the powder in water is known as **milk of lime, or lime slurry.** When reacting chemically, the soluble part reacts first; as this is used up more of the suspended solid dissolves and this in turn reacts. The action is therefore a progressive one. The final effect may be the same as with a stronger alkali, but the calcium hydroxide requires more time to react.

Calcium hydroxide is prepared by the action of water or steam on the anhydride, calcium oxide, CaO, known as **lime** or **quicklime.** This is obtained by heating limestone, $CaCO_3$, above 900° C. The operation is known as burning limestone and an old term for calcium oxide is **burnt lime.** Impurities which are apt to be present are iron, magnesium oxide, silica, and calcium carbonate from incomplete decomposition. Commercially lime is largely bought as the anhydride and slaked in water for use, rather than purchased as the more expensive hydrated lime. The commercial grades of lime are lump, ground and fine. Hydrated lime or calcium hydroxide is also an article of commerce. U.S.P. calcium hydroxide contains not less than 95 per cent of calcium hydroxide. The U.S.P. solution contains not less than 0.14 gram of calcium hydroxide per 100 cc., at 25° C.

Since lime slowly absorbs carbon dioxide from the air, some degree of protection is necessary. The ease with which lime can be slaked is controlled to a large degree by the conditions under which it was burned. Therefore it cannot be considered as standard in quality to the same extent as other alkalies and most other chemicals. Another important factor in its solution is the amount of magnesium oxide present, since some dolomitic limestone is burned, and the product may contain up to 30 per cent of magnesium oxide. This type of lime is not ordinarily offered as chemical lime but rather as builders' lime.

Slaked lime is used in the manufacture of more expensive alkalies from naturally occurring salts, such as in the lime-soda process for caustic soda. It is used in large amounts to neutralize acids in the chemical industry. It is particularly applicable for neutralization of sulfuric acid because the product of the reaction, calcium sulfate, is precipitated. In the manufacture of bleaching powder, chlorine is passed over trays of slaked lime. Combination occurs as represented by the formula, $CaCl(OCl)$, a double salt, a calcium chloride and hypochlorite. A straight hypochlorite, $Ca(OCl)_2$, is also produced from lime by another process. Lime mortar is made by slaking lime with water and mixing with sand in approximately the ratio of 1 part of 40 per cent lime slurry to

3 parts of sand, by volume. Usually some Portland cement is mixed with it before use. The mortar sets by the evaporation of the water and the reaction of calcium hydroxide with carbon dioxide in the air to form calcium carbonate. Cement, if added, assists in producing the set. A rigid structure is formed which acquires a high strength over a period of years. Similar mixtures are used as lime plaster, with the addition of fiber or hair in the undercoats. For a finish coat, hydrated lime slurry mixed with a minor amount of fine white sand is commonly applied.

Lime slurry is used in the purification of sugar juices to precipitate phosphates and carry down colloidal impurities in the sugar solution. Slaked lime is used to remove hair from hides preparatory to leather tanning, as a water softener, in whitewash, in water paints, for ammonia recovery in gas manufacture, in agriculture, and as an anti-acid in medicine. Lime soaps are prepared and used in lubricants and greases. Good-quality lime is the basic material for the manufacture of many calcium salts. Where applicable, lime is outstanding as the inexpensive industrial alkali. For spraying as an insecticide, hydrated lime is sold under the name **spray lime** or **lime spray,** a grade readily dispersible in water.

Barium hydroxide or **barium hydrate,** $Ba(OH)_2$, is a white powder. The dry material absorbs carbon dioxide readily from the air and must therefore be kept in tightly closed containers. The aqueous solution is weakly alkaline and is known as **baryta-water.** The solution also reacts readily with carbon dioxide in the air. The solubility of barium hydroxide differs from that of calcium hydroxide in that the former is moderately soluble in cold water and readily soluble in hot water. It is also soluble in alcohol.

Barium hydroxide can be prepared by dissolving the oxide, BaO, in water. An energetic reaction with water occurs to form the hydroxide. When a hot saturated solution of the hydroxide is allowed to cool, a hydrate crystallizes out, $BaOH,8H_2O$. Large-scale preparation of the hydroxide is carried out by heating a naturally occurring salt, barium sulfate or barytes, with carbon in the form of fine coal. Barium sulfite is obtained and is then heated in a current of moist carbon dioxide to form barium carbonate and hydrogen sulfide. The carbonate is then decomposed with a current of superheated steam to form the hydrate. Barium hydroxide is also prepared by electrolysis, starting with barium chloride solution and using a mercury cathode. Iron and calcium may be present in the less pure forms.

Because of the great insolubility of the sulfate, barium hydroxide is used in inorganic chemistry for semi-quantitative neutralization of sulfuric acid. It is used similarly for the precipitation of carbonates—in tanning for dehairing, and for the preparation of barium soaps for incorporation in lubricants. Former use in the sugar industry to neutralize organic acid impurities has largely been superseded by processes utilizing calcium or strontium hydroxide. It is the starting material for the preparation of many barium compounds.

CHAPTER IV

SODIUM SALTS OF INORGANIC ACIDS

Because of cheapness and ease of solubility in water sodium salts are the most widely used inorganic salts. The metal itself has practical application solely in organic reactions and that not in an aqueous medium because it reacts with water to generate hydrogen. The term soda is used loosely in commerce, sometimes in place of sodium, as in referring to soda sulfate when sodium sulfate is meant. More strictly, soda means sodium carbonate, known as soda ash. Occasionally the term soda solution is used to mean caustic soda solution, particularly when referring to foreign practice. When not otherwise indicated sodium compounds are white. They are soluble in water but generally insoluble in alcohol, unless otherwise noted.

Sodium, Na, is a white metal, so soft that it can be cut with a knife. While it has a silvery luster it reacts with moisture so readily that it shows a silvery sheen only when freshly cut. Sodium is stored under mineral oil to prevent access of moisture. Its reaction with water is so vigorous as to ignite the hydrogen generated in the reaction. It is sold in the form of bricks weighing about 12 pounds. Its electrolytic production from fused sodium chloride at a relatively low price permits its use for liberation of some of the more expensive metals, but not on a large scale. It is used rather widely in organic synthesis, for drying the best grades of ether, and for related purposes.

Sodium peroxide or **sodium dioxide,** Na_2O_2, is a yellowish powder, usually granular, and is very hygroscopic. It may be considered as the sodium salt of hydrogen peroxide, and when dissolved in acid with cooling, gives a dilute solution of hydrogen peroxide. This is of no practical importance. When added to water without cooling, oxygen is evolved and sodium hydroxide results. Sodium peroxide is produced by burning sodium in excess of air. Typical uses are as a powerful oxidizing agent, as a reagent in synthesis, and as a bleaching agent on resistant materials which will not be damaged by the alkalinity produced. The normal **sodium oxide,** or **sodium monoxide,** Na_2O, is of only theoretical importance.

Sodium carbonate, soda ash, or **calcined soda,** Na_2CO_3, is the manufactured compound of sodium handled in greatest tonnage. The usual commercial form is an anhydrous powder, but **soda monohydrate,** Na_2CO_3, H_2O, and the decahydrate, Na_2CO_3, $10H_2O$, are also sold. The latter is known as **sal soda,** or **washing soda.** Sodium carbonate is moderately soluble in cold water and very soluble in hot water. To a large extent the term sodium carbonate is used by chemists and the term soda ash in the trade. The aqueous solution is strongly alkaline, due to hydrolysis, and this is the basis for some of its uses.

The old process of manufacture known as the Le Blanc process used sodium chloride and sulfuric acid as starting materials. The sodium sulfate formed was reduced to the sulfide which reacted with limestone, calcium carbonate, to give sodium carbonate. This has been superseded by the ammonia-soda or Solvay process. In this a solution of sodium chloride, common salt, is saturated with ammonia gas, then carbon dioxide, obtained by heating limestone, is bubbled in at the bottom. The carbonic acid formed reacts with the ammonia and the product ammonium bicarbonate, reacts with sodium chloride to form sodium bicarbonate. This precipitates out and is separated from the liquid by filtration. Anhydrous sodium carbonate is obtained by heating the bicarbonate. Carbon dioxide is the by-product of this final reaction and is re-used in the process. Ammonium chloride from an earlier step reacts with lime from another earlier step to liberate ammonia for re-use. This leaves only calcium chloride as a by-product. Some is used, and the balance run to waste in aqueous solution. This is in sharp contrast to the Le Blanc process which rapidly built up dump piles of waste products.

The decahydrate is obtained by dissolving soda ash in water and recrystallizing. On exposure to dry air it loses water to give the monohydrate. This hydrate is also produced directly under suitable conditions.

Soda ash is sold to contain the equivalent of 58 per cent of sodium oxide, Na_2O, which corresponds to 99 per cent of soda ash. Dense, light and extra light grades are available, of which the dense grade commands a small premium because of the extra processing necessary. The hydrated forms cost relatively more because of the extra processing, when one considers that the monohydrate contains 85.6 per cent of soda ash and the decahydrate 37.1 per cent. Impurities present are salt and sodium bicarbonate. The latter results in part from absorption of carbon dioxide from the air. The U.S.P. monohydrate, $Na_2CO_3.H_2O$, contains 10-15 per cent of water, and not less than 99.5 per cent of anhydrous sodium carbonate on a dry basis. Soda ash is to be considered among the inexpensive alkalies, in the sense that it reacts to neutralize acid. The neutralizing value of 1 pound of soda ash equals that of about three-fourths pound of caustic soda, which sells for more than twice as much. Soda ash is fused with lime and sand to produce glass. Mixed with a small amount of soap and allowed to crystallize as the decahydrate, it forms the soap powders of commerce. Large amounts are used as soap builders with soap in laundering. Other uses are in water softening, processing of textiles, etc. A major use is for production of other sodium salts.

Sodium bicarbonate, sodium acid carbonate, or **baking soda,** $NaHCO_3$, is moderately soluble in cold water and much more soluble in hot water. Its aqueous solution is mildly alkaline even though structurally it is an acid salt of carbonic acid. It is produced as an intermediate product in the Solvay process for manufacture of soda ash. It is sold in granular and powdered forms, and in C.P. and U.S.P. grades. The latter contains not less than 99 per cent of sodium bicarbonate. It tends to give off carbon dioxide to form a minor amount of sodium carbonate on exposure to air. It is used as an ingredient of baking powder and effervescent medicinals, where by reaction with an acid, it liberates the necessary gas, carbon dioxide. For these uses it is more suitable than soda ash because the bicarbonate requires less acid to decompose it. Its mild alkalinity finds many other applications.

Sodium sulfate, Na_2SO_4, is a crystalline compound moderately soluble in cold water and very soluble in hot water. By solution in water and recrystallization, **Glauber's salt** or **sodium sulfate decahydrate,** $Na_2SO_4, 10H_2O$, is manufactured. The U.S.P. decahydrate contains 51-57 per cent of water and not more than 1 per cent of impurities. The anhydrous salt occurs naturally. Both the anhydrous form and the hydrate are produced as by-products of various industries such as in the manufacture of hydrochloric acid from common salt and sulfuric acid, by further processing of the crude **salt cake,** which is largely sodium sulfate. Both forms are quoted and much Glauber's salt is imported. Slightly over 0.44 pound of the anhydrous salt is equivalent to 1 pound of Glauber's salt. On a basis of actual chemical content the latter form commands a substantial premium because of its ease of solution and perhaps because of custom in its use. The anhydrous form is an important ingredient of glass. Both are used in dyeing, although Glauber's salt more commonly. The crude salt cake also has a market although it contains only 92-98 per cent of sodium sulfate with impurities such as bisulfate, calcium, iron, magnesium and silica.

Chrome cake is a green form of salt cake, sodium sulfate, containing a small amount of chromium as a natural impurity, which is the source of the coloring matter. It is a by-product in the manufacture of bichromates and is much cheaper than the usual salt cake. Its use is largely in the paper industry.

Sodium bisulfate, or **sodium acid sulfate,** $NaHSO_4$, is a crystalline material moderately soluble in cold water and very soluble in hot water. It is, as the structure implies, acid in reaction when in aqueous solution. A major source is as a by-product in the manufacture of volatile acids by heating their sodium salts with excess sulfuric acid. That obtained from such treatment of sodium nitrate is known as **niter cake.** In the crude form it may contain residual salts such as sodium nitrate, arsenic, heavy metals and potassium salts. Sodium bisulfate is used as a flux for iron and steel, as a controlled acid reagent in dye baths, and in general as a mildly acid buffered ingredient at a low price per pound. For example, a popular cleaner for automobile radiators and vitreous porcelain consists of this compound with minor added ingredients. Its sale is controlled by the Caustic Poison Act, given in Appendix A.

Sodium sulfite, Na_2SO_2, is the salt of sulfurous acid and is moderately soluble in cold water, very soluble in hot water. The hydrate, $Na_2SO_3,7H_2O$, is prepared by saturating a solution of soda ash with sulfur dioxide, adding another equivalent of soda ash and crystallizing. The anhydrous salt is prepared by heating the hydrated salt. Both the anhydrous or powder form, and the hydrated or crystalline form are sold. The latter contains 50 per cent of the anhydrous salt. Because the anhydrous material must be prepared from the hydrate the latter costs less on a basis of chemical content. Its general uses are as a reducing agent and as a source of sulfur dioxide when added to strongly acid solutions. Thus it is used in the textile industry as an antichlor and in photography. Its use as a preservative in foodstuffs is permissible to only a limited extent when declared on the label.

Sodium bisulfite or **sodium acid sulfite,** $NaHSO_3$, is obtained by saturating a caustic soda solution with sulfur dioxide. The product actually obtained in solid form is usually a double salt, **sodium metabisulfite,** $Na_2S_2O_5$, which is the dehydration product of two molecules of sodium bisulfite. The product is also sold as solutions of 32°, 33°, 35° and 40° Baumé, containing respectively 35, 36.25, 38.78 and 44.92 per cent of the product. The solutions are more convenient to use but more expensive. It is used as a reducing agent in many industries such as in the manufacture of leather and paper, as a photographic chemical and to some extent, as a food preservative, although its use for this purpose is strictly limited by law.

Sodium thiosulfate or **"hypo,"** $Na_2S_2O_3$, $5H_2O$, is extremely soluble in hot or cold water. The product is sold in the trade under an old name of sodium hyposulfite which is more correctly that of another chemical, $Na_2S_2O_4.2H_2O$. Confusion often arises, even among chemists. The photographers' "hypo" is the thiosulfate. It is prepared by boiling a solution of sodium sulfite with sulfur. It forms beautiful large crystals and is sold as granular, pea-size and large. The U.S.P. pentahydrate contains 32-37 per cent of water, and not less than 99 per cent of the pure salt on a dry basis. Its uses are for dissolving silver salts as in photography, in the extraction of silver from its ores, and as an antichlor to destroy free chlorine; also as a textile chemical, and in synthetic organic chemistry as a rather mild reducing agent. This is in contrast to the chemical properly called sodium hyposulfite or in the trade sodium hydrosulfite, which is a powerful reducing agent.

Sodium hyposulfite, or sodium hydrosulfite, $Na_2S_2O_4, 2H_2O$, is a powerful reducing agent, very soluble in cold water and decomposed by hot water. The name is often confused with an old name for sodium thiosulfate which is still quoted in the trade as sodium hyposulfite. This material is, however, the one which correctly bears that name. It is formed by the action of zinc on sodium bisulfite and sulfurous acid. Zinc sulfite precipitates leaving the hydrosulfite in solution. This is then precipitated by adding salt to the filtered solution. While at one time available only in solution the solid is now also sold. Its uses relate largely to discharge of dyestuffs as in textile printing.

Sodium sulfide, Na_2S, while obtainable in clear, transparent crystals, is usually colored yellow by polysulfides. It is very deliquescent and is moderately soluble in cold water, very soluble in hot water and slightly soluble in alcohol. It is manufactured by saturating a caustic soda solution with hydrogen sulfide, then adding another equivalent of alkali. In a less pure form it is obtained by heating sodium bisulfate and coal. It is sold as 80 per cent crystals and 60 or 62 per cent solid, flakes or chips. Sodium sulfide is a powerful reducing agent and finds use in the synthetic manufacture of dyes and in such industries as those of rayon, metallurgy, photography and engraving.

Sodium chloride, salt, rock salt, common salt,or **halite,** $NaCl$, is very soluble in hot or cold water. It occurs naturally in various parts of the world. In some places it contains up to 5 per cent of impurities such as calcium, magnesium and iron, while in this country salt deposits are unusually pure. In some places it is mined, in others wells are drilled and the salt dissolved with water and pumped to the surface. It is purified where necessary by solution, filtration and crystallization. Recovery from sea-water is of more historical than practical importance.

Rock salt is a coarse grade. Crystals of all degrees of fineness are obtainable. The removal of the last traces of impurity is expensive and only carried out when essential. Impurities of calcium or magnesium chloride cause caking unless powdered chalk or tricalcium phosphate is added to prevent it. The U.S.P. grade contains not less than 99.5 per cent of sodium chloride, when dried to constant weight. Pure grades of rock salt are used in the dairy and pickle industries and for grinding and sieving to a fineness suitable for table salt. For table use iodides are often added. Less pure forms are used in fish curing, meat packing, refrigeration, curing hides, etc. Some concept of the magnitude of use of salt can be gleaned from the fact that it is the essential starting material for the manufacture of nearly all sodium compounds, and the source of nearly all of our chlorine. Chlorine is produced directly, sodium compounds through the intermediate stages of soda ash or caustic soda.

Sodium bromide, $NaBr$, is very soluble in water. It is obtained by the reaction of ferrosoferric bromide and soda ash in solution. Its main uses are as the highly purified salt in photographic emulsions and in medicine.

Sodium iodide, NaI, is extremely soluble in water. It is prepared from ferrosoferric iodide, obtained by the reaction of iron, iodine and water. The ferrosoferric iodide reacts with soda ash to give sodium iodide, which is recovered from solution after filtration. The U.S.P. grade contains not more than 5 per cent of water, and not less than 99 per cent of sodium iodide when dried to constant weight. It is mainly used as a very pure grade in medicine, and in preparing photographic emulsions.

Sodium fluoride, Na_2F_2, is moderately soluble in water. It is obtained by the reaction of soda ash with hydrofluoric acid. Arsenic and soda ash may be present as impurities. Grades are 90 and 95 per cent. It is largely used as an insect and rat poison.

Sodium bifluoride or **sodium acid fluoride,** $NaHF_2$, is the water-soluble acid salt of sodium fluoride. It is used as an etching agent, as a preservative for specimens of organic nature, as a "sour" in laundering and in various other ways as a mildly acid ingredient.

Sodium silicofluoride or **sodium fluosilicate,** Na_2SiF_6, is a salt which is moderately soluble in water. Its solution is acid due to slight hydrolysis to sodium fluoride, silicic acid and hydrofluoric acid. This reaction goes on progressively in the presence of any basic material. It is formed by neutralization of fluosilicic acid with soda ash, the fluosilicic acid being a by-product of the phosphorus and phosphoric acid industry. A substantial part of that used in the United States is imported. Its use, aside from medicine, is as a mild neutralizing agent, such as in laundry and textile sours, in the hardening of cement, setting of silicate cements, etc.

Sodium hypochlorite, $NaOCl$, is not sold as a solid chemical nor under its chemical name. An aqueous solution is sold as **bleach liquor, chlorine bleach,** or **Javelle water.**. This is manufactured by passing chlorine gas into a well cooled solution of caustic soda. It is customarily sold at about 10 per cent available chlorine content. The solution always contains excess caustic soda and is therefore strongly alkaline. It is handled in glass carboys and glass-lined tank cars. Therefore local supplies are preferred. because of the cost of transportation. A U.S.P. solution contains 4-6 per cent of sodium hypochlorite. For household use a similar product is merchandised with about a 5 per cent available chlorine content, and excess alkali as carbonate. Uses are for bleaching of textiles, general sterilization, disinfection, etc. Its sale is subject to the Caustic Poison Act, given in Appendix A. In the cotton textile industry the solution is not purchased as such but chlorine is passed into the kier containing the cotton fabric and caustic soda solution, to produce the sodium hypochlorite. Diluted to 0.5 per cent available chlorine it is **Dakin's solution,** which finds a wide use as an antiseptic. In a U.S.P. grade, this solution contains 0.45-0.50 gram of sodium hypochlorite per 100 cc. of solution, which is equivalent to 0.43-0.48 gram of available chlorine.

Sodium chlorate, $NaClO_3$, is very soluble is cold water, extremely soluble in hot water and soluble in alcohol. It is obtained by heating and electrolyzing a concentrated solution of sodium chloride and caustic soda or by passing excess of chlorine into hot caustic soda solution. The product crystallizes on cooling. It is used as a strong oxidizing agent, particularly in solution with acids. It is less expensive than potassium chlorate and 0.87 pound of the former is as effective as 1 pound of the potassium compound. A typical use is in the liberation and recovery of bromine and iodine from their salts.

Sodium iodate, $NaIO_3$, is an oxidizing agent similar in properties to sodium chlorate but milder in action. It is not competitive in price. It is moderately soluble in cold water, very soluble in hot. Sodium iodate is recovered from crude Chile saltpeter and is formed by the reaction of iodine with sodium chlorate in the presence of nitric acid. Its use is largely in medicine.

Sodium nitrate, $NaNO_3$, is very soluble in cold water and extremely soluble in hot. It is also soluble in alcohol and glycerine. The salt occurs naturally as **Chile saltpeter.** The crude salt is extracted with water, filtered and recrystallized. Modern processes of nitrogen fixation permit its synthetic manufacture, and some may be produced by the arc process. Both crude and refined grades are sold, the latter in either granular or powdered forms. The crude as quoted is about 92 per cent pure. Because of the great importance of nitrates as fertilizers, its use is fundamental in that industry. It is also used as a basis of production of nitric acid by treatment with sulfuric acid, giving niter cake as a by-product—to manufacture potassium nitrate and sodium nitrite, and as a flux. Its use as a source of nitrogen is constantly declining, having fallen from two-thirds of the world's fixed nitrogen supply to only 7 per cent, in the past 35 years.

Sodium nitrite, $NaNO_2$, is soluble in the same solvents and to about the same extent as the nitrate. It is obtained by heating sodium nitrate, which gives up oxygen. The process is aided by the presence of lead which combines with the oxygen as the nitrate decomposes. The sodium nitrite is extracted with water and recrystallized. Impurities such as potassium salts, chlorides, iron and sulfates may be present. The commercial uses do not require a high degree of purity so that a 96-98 per cent grade is quoted. The U.S.P. grade contains not less than 95 per cent of sodium nitrite when dried to constant weight. The uses are as a diazotizing agent in the preparation of dyes, and as a general reducing agent.

Sodium phosphate, even when limited to **sodium orthophosphate,** is a term which might refer to any of three salts. These differ according to the number of hydrogen atoms that have been neutralized in orthophosphoric acid. **Monosodium phosphate, primary** or **monobasic sodium phosphate,** NaH_2PO_4, is a slightly acid salt which is very soluble in cold water and extremely soluble in hot. It is obtained by mixing the correct amount of disodium phosphate and phosphoric acid, and concentrating to permit the salt to crystallize. Although it forms a monohydrate, the commercial product is anhydrous. Because its major uses are in medicine and in baking powder the grade is of high purity.

The second of the sodium salts of orthophosphoric acid is **disodium phosphate, secondary sodium phosphate,** or **dibasic sodium phosphate,** $Na_2HPO_4, 12H_2O$. It is moderately soluble in cold water and infinitely soluble in hot because of its low melting point, 34.6° C. It may be obtained from dicalcium phosphate by reaction with soda ash. The less soluble calcium carbonate precipitates, leaving disodium phosphate in solution, from which it can be crystallized. It is also the product of reaction of phosphoric acid and soda ash, the latter not being sufficiently alkaline to neutralize the acid further. A technical grade is sold as the hydrate. U.S.P. disodium phosphate as the heptahydrate, $Na_2HPO_4,7H_2O$, contains 43-50 per cent of water, and not less than 98 per cent of the anhydrous salt on a dry basis. U.S.P. anhydrous disodium phosphate contains not less than 98 per cent of the pure salt at constant weight. Although structurally an acid salt its aqueous solution is mildly alkaline. Typical uses are in the production of fertilizers, dyes, and pigments, and in textile processing.

The most alkaline salt of orthophosphoric acid is **trisodium phosphate, tertiary** or **tribasic sodium phosphate,** $Na_3PO_4, 12H_2O$. Although only moderately soluble in cold water it is very soluble in hot. It is obtained by neutralizing orthophosphoric acid as far as possible with soda ash, to give the dibasic compound, and then neutralizing the last hydrogen atom with caustic soda. As would be expected from this method of manufacture, its aqueous solution is strongly alkaline, more alkaline than a solution of soda ash of similar concentration. Usually some excess caustic soda is present as an impurity. The uses are numerous but none is outstanding. Typical ones are as water softener, soap builder and in metal cleaning.

Sodium pyrophosphate, or **tetrasodium pyrophosphate,** $Na_4P_2O_7$, is a salt moderately soluble in cold water and very soluble in hot water. It is formed by fusing disodium phosphate, when water is driven off. Disodium phosphate may be present as an impurity. The anhydrous salt may be dissolved in water and recrystallized to form the decahydrate, $Na_4P_2O_7,10H_2O$. A partially neutralized compound from lesser heating is **acid sodium pyrophosphate or disodium pyrophosphate,** $Na_2H_2P_2O_7$, $6H_2O$. The other two theoretical acid salts do not exist. The fully neutralized compound is sold in anhydrous and hydrated forms but the former, while it dissolves in water more slowly, is more economical. The acid salt is sold only as the hydrate. Uses are largely in water softening because the soluble calcium and magnesium salts are formed and prevent formation of calcium and magnesium soaps. This application and the corresponding application of sodium metaphosphate is referred to industrially as **calcium sequestration.**

Sodium metaphosphate exists in two forms. The older form, $Na_4P_4O_{12}$ has but little use because of its water insolubility. A water-soluble form, $NaPO_2$, is available and is often referred to by the longer term of **sodium hexametaphosphate.** The method of manufacture is probably by controlled heating of monosodium orthophosphate to drive off water. The material is sold as flakes, either alone or with added soda ash to increase the alkalinity. Its use is mainly for softening water for the same reasons as given for the pyrophosphate.

Sodium hypophosphite, NaH_2PO_2, H_2O, is a salt soluble in alcohol or water, obtained by neutralizing hypophosphoric acid with soda ash. It is used in medicine as a source of assimilable phosphate.

Sodium silicate is a term applying to a series of compounds ranging in properties from strongly alkaline to nearly neutral, from crystalline to glassy solids. The most alkaline is **sodium orthosilicate,** Na_4SiO_4, an amorphous form prepared by heating silica or lower silicates with sodium hydroxide. It is used in metal cleaning and as a general, strongly alkaline detergent.

Sodium sesquisilicate, Na_4SiO_4, Na_2SiO_3, $11H_2O$, is intermediate in composition between the orthosilicate and the metasilicate. It is crystalline and is prepared much the same as the orthosilicate but is crystallized from solution. It is used for the same purposes as the ortho compound. Being milder, it is also used for purposes for which the orthosilicate is too drastic.

Sodium metasilicate, Na_2SiO_3, is one of the oldest of the known definite silicates. It exists as several hydrates, the pentahydrate and hexahydrate being common. Its uses are similar to those of the preceding silicates but it is milder in its action. Even then it is more alkaline than soda ash or trisodium phosphate. It is prepared by fusion of silica and soda ash or by adding sodium hydroxide to solutions of the lower silicates. One other silicate of definite composition is known, **sodium acid silicate,** $NaHSiO_3$. It exists as a spray-dried solid as well as in solution.

The remaining grades of sodium silicates cover a range of compositions without being definite compounds. They are usually expressed by their ratio of $Na_2O:SiO_2$. In these terms the more silicious silicates range downward from 1:1 to 1:4. In the same terms the orthosilicate is 2:1, the sesquisilicate 1½:1 and the metasilicate 1:1. The lower silicates are usually sold in solutions containing 20-50 per cent of dissolved solids. They are often called **waterglass** which is therefore of indefinite composition. They are quoted by Baumé readings and are turbid rather than clear solutions. The lower silicates are also sold in solid form but the solid dissolves in water only very slowly. These silicates are used as fireproofing agents, as adhesives, for production of higher silicates, in ceramic glazes, as a builder in soaps, as detergents, as deflocculating agents in clays, as sizings and for numerous miscellaneous purposes. The variation in use of the higher to lower silicates from metal cleaners to adhesives strikingly illustrates the range of properties involved and the indefiniteness of the term sodium silicate unless defined by a ratio of $Na_2O:SiO_2$.

Sodium cyanide, NaCN, is the sodium salt of hydrocyanic or prussic acid. It is soluble in cold water, very soluble in hot water and soluble in alcohol. One method of manufacture is by fusion in an electric furnace of calcium cyanamide, sodium chloride and a little calcium carbide. Another method is to melt metallic sodium with charcoal and blow dry ammonia gas into the molten material. Sodamide is first formed, changed to cyanamide, then to cyanide. Formamide is decomposed by heat and the presence of a catalyst into hydrocyanic acid, which reacts with caustic soda to form sodium cyanide. Hydrocyanic acid may be produced in other ways as by the arc process, and used for the manufacture of sodium cyanide. While a C.P. grade of this salt is available the bulk used is of technical 96-98 per cent grade. Both imported and domestic sources supply the market. Uses are mainly in gold extraction, in case-hardening of steel and in electroplating. For fumigation with hydrocyanic acid the sodium salt is sometimes used, being treated with sulfuric acid to liberate the hydrocyanic acid.

Cyanide-chloride mixture is a mixture of about 75 per cent sodium cyanide and 25 per cent sodium chloride, sold in granular or lump form for case-hardening of steel.

Case-hardening mixture is sodium cyanide diluted with sodium chloride and sodium carbonate, used for case-hardening of steel. Grades contain 30, 45 or 60 per cent sodium cyanide, and are sold in lump and granular forms.

Sodium thiocyanate, or **sodium sulfocyanide,** $NaCNS$, is very soluble in water or alcohol. It is obtained as deliquescent crystals by boiling sodium cyanide with sulfur. Uses are in dyeing textiles and in medicine.

Sodium ferrocyanide, or **yellow sodium prussiate,** $Na_4Fe(CN)_6,12H_2O$, is a yellow salt, very soluble in water. While a derivative of hydrocyanic acid, it is not poisonous. One source is by treatment of the spent oxide from illuminating gas. Water and carbon bisulfide are used to remove soluble salts and sulfur from the oxide. The residue is heated with lime to give ammonia and calcium ferrocyanide. Salt is added to an aqueous extract of the calcium salt, and soda ash to precipitate calcium. The solution of sodium ferrocyanide is filtered and crystallized. It is not particularly difficult to get a reasonable degree of purity. Uses are as a mild reducing agent in the synthetic organic chemical industry, for manufacture of ferricyanides and for various miscellaneous purposes.

Sodium arsenate, $Na_3AsO_4,12H_2O$, is a salt of arsenic which is very soluble in water, and slightly soluble in alcohol. It is prepared by heating arsenic trioxide and sodium nitrate together and recrystallizing from water. The hydrated salt is sold for making other arsenates, particularly lead arsenate, and for use directly in insecticides. It is also used to some extent in the textile industry as an assist in dyeing and printing. Like all soluble arsenic compounds it is very poisonous.

Sodium arsenite is the salt of arsenious acid. The structure is $NaAsO_2$ instead of that of the theoretical ortho salt Na_3AsO_3. Therefore it is also called **sodium metaarsenite.** It is very soluble in cold water, slightly soluble in hot and somewhat soluble in alcohol. It is obtained by direct reaction of arsenic trioxide, the anhydride of arsenious acid, with caustic soda. The salt is strongly hydrolyzed in aqueous solution to give an alkaline reaction. This is basically the reason why arsenates are made from arsenites as the medium for application of arsenic for many insecticidal purposes. Commercial grades are designated as white and gray, the latter being less pure and selling at a lower price. Sodium arsenite is also sold in solution. Uses are in a few insecticides, in medicinal soaps where alkalinity would not be objectionable, and as an antiseptic and preservative. Like all soluble arsenic compounds it is very poisonous.

Sodium antimonate or **sodium pyroantimonate,** Na_2SbO_3, $7H_2O$, occurs as colorless crystals, slightly soluble in water or alcohol. The salt is formed by the reaction of antimony hydroxide and sodium hydroxide. It is used mainly for production of opaque glass or enamels and therefore sold in a somewhat impure technical grade. Antimony compounds approach those of arsenic in poisonous properties.

Sodium bichromate, or **sodium dichromate,** $Na_2Cr_2O_7$, $2H_2O$, is an inexpensive salt containing chromium in a soluble form, being very soluble in cold water and extremely soluble in hot. Structurally it is **sodium acid chromate,** $NaHCrO_4$, of which two molecules have united with the loss of a molecule of water. It is prepared by fusing chrome iron ore with lime and soda ash in the presence of air. The product is extracted with water and acidified with sulfuric acid. After filtration and concentration of the filtrate, the salt crystallizes. Chemically it behaves like an acid salt. It is used in many processes as an oxidizing agent. Mixed with sulfuric acid it is the equivalent of chromic acid and is less expensive than the acid alone.

It is the starting material for preparing nearly all chromium salts. Reduced to the basic chromate it is used in tanning. As an oxidizing agent it is used to bleach oils and fats, in chrome dyeing, in dye manufacture and in many other industries. Completely neutralized and crystallized sodium bichromate gives **sodium chromate,** Na_2CrO_4, 10 H_2O, soluble in water and slightly soluble in alcohol. Sodium chromate is used as a mordant and in the manufacture of pigments.

Sodium stannate, Na_2SnO_3, $3H_2O$, is a grayish or white hygroscopic material, extremely soluble in cold water and moderately soluble in hot. It is a salt in which tin acts as an acidic rather than as a basic element, hence its solutions are strongly alkaline. Both the salt and its solutions absorb carbon dioxide from the air. It is obtained by fusing stannic oxide with caustic soda or by boiling tin scrap with sodium plumbate, which is a solution of lead oxide in caustic soda. Its main uses are as a mordant in the textile industry and in fireproofing textiles.

Sodium tetraborate, sodium borate, or **borax,** $Na_2B_4O_7$, $10H_2O$, is slightly soluble in cold water, extremely soluble in hot and also soluble in glycerine. It is a naturally occurring product which is purified by crystallization, to give varying grades. Borax is also obtained from naturally occurring calcium borate by fusion with sodium carbonate and extraction with water of the more soluble sodium borate from the residual calcium carbonate. Other sodium borates exist besides borax but are less common. Borax is an alkaline salt, hydrolyzing in aqueous solution to give a slightly alkaline reaction. In addition to U.S.P., quotations cover powdered, granular and technical 99½ per cent grades. U.S.P. borax contains 52.32-54.92 per cent of anhydrous sodium tetraborate, $Na_2B_4O_7$, corresponding to not less than 99 per cent of the decahydrate, $Na_2B_4O_7$, $10H_2O$. **Anhydrous borax** or **borax glass** is also produced. The uses are very numerous. As a preservative borax is not permitted in food products. It is used in medicine as a mild antiseptic. Other uses are in ceramics, glass, glazes, solders, detergents, fluxes, as a water softener, etc.

Sodium perborate is a mild oxidizing agent in water, in which it is moderately soluble. It forms two hydrates, $NaBO_3.H_2O$ and $NaBO_3,4H_2O$ of which the latter is the usual commercial form. It is prepared by heating borax, sodium peroxide and hydrogen peroxide in aqueous solution. Sodium perborate crystallizes out on cooling. It may also be prepared from boric acid and sodium peroxide in acid solution. The usual grade is N.F. The U.S.P.

grade contains not less than 9 per cent of available oxygen corresponding to about 86.5 per cent of the tetrahydrate, $NaBO_3,4H_2O$. It is used as an oxidizing and bleaching agent, antiseptic and deodorant, such as in soap products, cosmetics, textile processing, etc. It is often recommended as an oral antiseptic because of its mild oxidizing effect on anaerobic bacteria in the mucin plaque on the teeth and for assistance in removal of mucin deposits.

Sodium molybdate is the chemical name for a whole series of compounds ranging from $NaMoO_4$ to $NaMo_{10}O_{31}$. Commercially the normal compound $NaMoO_4$ or $NaMoO_4,2H_2O$ is meant. It is extremely soluble in hot or cold water and is prepared by the reaction of molybdic acid and caustic soda. Both the anhydrous and dihydrate salts are quoted as technical products. It is used in casein adhesives, in medicine and in the preparation of pigments.

Sodium tungstate, $NaWO_4,2H_2O$, is extremely soluble in hot or cold water but reacts with acids to form insoluble tungstic acid. It is obtained by dissolving tungsten trioxide or tungstic acid in caustic soda solution. Grades are C.P. and technical. It is used to produce other tungsten compounds, as a fireproofing agent and for precipitation of proteins.

CHAPTER V

POTASSIUM SALTS OF INORGANIC ACIDS

Potassium as a metal is similar to sodium. With rare exceptions potassium and sodium salts can be used alternatively. In that case the sodium compound is usually preferable on a price basis. If used for the negative radical such as sulfate or chromate, a pound of sodium compound will give more value than a pound of the equivalent potassium compound, always providing that the former is not more highly hydrated.

Since the practical application of inorganic chemistry largely originated in Europe where potassium salts are plentiful, there are still many uses to which potassium compounds are put, more because of past custom than because of greater merit. This naturally appertains more to small-scale work than to large-scale use.

Potassium salts are sometimes incorrectly listed as potash salts. Potash is the commercial term applied to potassium carbonate, but like "soda," it is rather loosely used. In the fertilizer industry potash content refers to potassium oxide, K_2O, content. Yet another meaning occasionally encountered is the use of "potash" or "potash lye," meaning caustic potash. This is similar to a trade use of the term "soda" or "soda lye." Except where otherwise indicated, potassium salts are white. As a class, they are water-soluble.

Potassium, K, is a silvery metal closely related to sodium in properties but somewhat less reactive with water. It is produced by methods analogous to those for sodium, but is of little commercial importance.

Potassium carbonate, potash or **pearl ash,** K_2CO_3, K_2CO_3,H_2O, or $2K_2CO_3,3H_2O$, is the very soluble salt of potassium corresponding to soda ash. The aqueous solution is strongly alkaline. It is made for the most part from potassium chloride. The natural salt is heated with magnesium carbonate, water and carbon dioxide under pressure, to give a mixed carbonate of potassium and magnesium. This is decomposed by heat and the potassium carbonate recovered from the filtrate, after precipitated magnesium carbonate has been filtered off. It can be made by the equivalent of the ammonia-soda process. Historically, the salt was obtained from the leaching of wood ashes. Sulfates, chlorides and some insoluble matter are present in the crude product. The purest grade is obtained by igniting pure bicarbonate.

Potassium carbonate is highly hygroscopic. Because of its medicinal use, U.S.P. granular and powdered grades are quoted, containing from 1.0 to 15 per cent of water, or a minimum of 99 per cent of pure anhydrous salt when dried to constant weight. The calcined salt at 99-100 per cent and the hydrated salt at 83-85 per cent are articles of commerce. Because of high solubility, solutions are also sold. Potassium carbonate is the basic material for preparation of many potassium salts. Other uses are in special glasses and as a dehydrating agent.

Cottonseed hull ash is obtained by ashing the outer covering separated from cottonseeds. The potassium is present as carbonate. It is sold to contain 25-30 per cent of potash, meaning potassium oxide, and is used in mixed fertilizers. Several other forms of ash, such as **rice hull ash,** are similarly sold but are not commonly or regularly quoted.

Potassium bicarbonate or **potassium acid carbonate,** $KHCO_3$, is very soluble in water but much less soluble than the carbonate. It is precipitated by passing carbon dioxide through a strong solution of the normal carbonate. If silicate is present, it is necessary to remove precipitated silica. Potassium carbonate may be recovered by recrystallization from the filtrate. The bicarbonate is also obtainable by the equivalent of the ammonia-soda process. The U.S.P. grade is sold in crystalline and granular forms and contains 99-100 per cent of potassium bicarbonate. It is largely used in medicinal products.

Potassium sulfate, K_2SO_4, is moderately soluble in cold water and very soluble in hot. It can be made by treating potassium chloride with sulfuric acid and calcining. The residue is readily purified by crystallization. N.F. and technical 90-95 per cent grades are sold. It is used mainly for preparing alums, in the manufacture of special glasses, and in the preparation of other potassium salts. **Potassium magnesium sulfate** is quoted as such with a 48-53 per cent potassium sulfate content, for use as fertilizer. Potassium sulfate forms a whole series of double salts known as **alums** of which **potash alum,** K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$, is typical. In this the potassium may be replaced by any other monovalent metal such as sodium or ammonium and the aluminum by other trivalent metals such as ferric iron, chromium, etc. The alums are relatively unimportant except where high purity is required. Simple sulfates are cheaper on a basis of the active material desired. In general alums are discussed with the sulfates of the heavy metal characterizing the individual alum.

Potassium bisulfate or **potassium acid sulfate,** $KHSO_4$, is very soluble in cold water, extremely soluble in hot and reacts with alcohol. It is prepared by fusing 13 parts of the normal salt with 8 parts of sulfuric acid. In solution it behaves as though the normal salt and sulfuric acid were present uncombined. Chlorides, heavy metals and arsenic may be present as impurities. Potassium bisulfate is used as a flux, in the production of bitartrates and where an acid salt of potassium is needed. Its sale is controlled by the Caustic Poison Act, given in Appendix A.

Potassium metabisulfite, $K_2S_2O_5$, is a water-soluble salt obtained by treating a hot saturated solution of potassium carbonate with sulfur dioxide, or a mixture of milk of lime and potassium sulfate with sulfur dioxide. It is used in moderate amounts for the same purposes as sodium bisulfite.

Potassium nitrate, niter or **saltpeter,** KNO_3, is moderately soluble in cold water and extremely soluble in hot. It is made from Chile saltpeter by the double decomposition of the sodium nitrate with potassium chloride. On heating, sodium chloride precipitates and can be filtered off, and potassium nitrate crystallizes from the cold filtrate. Varied grades are sold such as powdered, granular and double-refined crystals. The crude material is used in fertilizers. Good-quality material is used as a preservative as in "corning" beef, pickling ham, etc. The U.S.P. grade, containing 99-100 per cent on a dry basis, is used in medicine. This salt is not deliquescent, while the corresponding sodium salt is moderately so. Therefore in the manufacture of pyrotechnics, matches, gunpowder, etc., from nitrates, the potassium salt must be used.

Potassium chloride or **potassium muriate,** KCl, is extremely soluble in cold water, very soluble in hot, and soluble in alcohol. It was formerly obtained mainly from the Stassfurt deposits where it occurs in such forms as **kainite,** $MgSO_4,MgCl_2,K_2SO_4,6H_2O$ and **schoenite,** $MgSO_4,K_2SO_4,6H_2O$. When a solution of the natural salts is treated with hydrogen chloride, potassium chloride is precipitated and magnesium and calcium chlorides and sulfates remain in the mother liquor. Competitive sources of potassium compounds are now worked in other countries, such developments having been stimulated by the World War. The crystalline product closely resembles common salt in properties and appearance.

A 98 per cent technical grade of potassium chloride is quoted and is used in the preparation of other potassium compounds as well as in fertilizers. Under the name of potassium muriate it is sold for fertilizer purposes, being quoted in both foreign and domestic grades at 50 per cent K_2O or 80 per cent KCl. Kainite and schoenite are also sold for their potassium values and as sources of magnesium compounds. Yet another fertilizer form is **potash manure salt,** a double salt of potassium and magnesium containing potassium carbonate, magnesium sulfate and a low proportion of chloride. The domestic product is sold as 25 and 30 per cent K_2O and the imported as 20 and 30 per cent K_2O. In contrast to sodium chloride, potassium chloride in its varied forms is marketed largely as a fertilizer ingredient.

Potassium bromide, KBr, is slightly soluble in alcohol, very soluble in cold water and extremely soluble in hot water. It is obtained by first forming iron bromide by the reaction of bromine water on iron filings. The iron bromide is allowed to react with potassium carbonate, the solution filtered, and the filtrate concentrated to crystallize potassium bromide. It is purified to U.S.P. grade containing 99-100 per cent on a dry basis, and is used in preparing photographic emulsions, in engraving and in medicine.

Potassium iodide, KI, is extremely soluble in cold water and even more soluble in hot. It is formed together with some potassium iodate, when iodine is dissolved in potassium hydroxide solution. The reaction mixture is evaporated to dryness and heated with powdered charcoal to reduce the iodate to iodide. It is then recrystallized. The U.S.P. grade contains 99-100 per cent of pure potassium iodide on a dry basis. Uses are in medicine and in the preparation of photographic emulsions.

Potassium chlorate, $KClO_3$, is slightly soluble in alcohol, moderately soluble in cold water and very soluble in hot water. It is obtained by passing chlorine into a warm saturated solution of lime water and adding potassium chloride. Potassium chlorate crystallizes from the solution on cooling. Another method is the electrolysis of a solution of potassium chloride in a suitable cell. Potassium chlorate is an active oxidizing agent. Crystalline, granular and powdered forms are sold. It is used in various ways as a powerful oxidizing agent, as in the manufacture of pyrotechnics, matches, fireworks and explosives. The U.S.P. grade contains 99-100 per cent, and is used in medicine.

Potassium perchlorate, $KClO_4$, is an even more powerful oxidizing agent than potassium chlorate. It is slightly soluble in cold water and alcohol, but very soluble in hot water. Gently heating potassium chlorate converts it to potassium perchlorate and potassium chloride. The potassium chloride is extracted with a minimum of water. Potassium perchlorate is used for purposes similar to those outlined for the chlorate.

Potassium iodate, KIO_3, is moderately soluble in cold water but very soluble in hot. It is formed by the action of iodine on potassium chlorate in the presence of nitric acid, and is used in medicine.

Potassium chromate, K_2CrO_4, is a yellow salt, very soluble in cold water and even more soluble in hot. It is the neutral chromate. Roasting ferrous chromite with potash and limestone forms potassium and calcium chromates. The latter is changed to potassium chromate by reaction with potassium sulfate solution, calcium sulfate being precipitated. Potassium chromate is used as a mordant for dyestuffs, in finishing leather and for various miscellaneous purposes.

Potassium permanganate, $KMnO_4$, is a deep purple crystalline salt moderately soluble in cold water and very soluble in hot. Even very dilute solutions are purple to violet in color. Potassium manganate is first prepared by fusing potassium carbonate and potassium nitrate with an oxide of manganese. This is then decomposed in acid solution, with precipitation of manganese dioxide and formation of potassium permanganate which is crystallized from the filtrate. It is an oxidizing agent in both alkaline and acid solution but the reactions are different in the two cases. In acid solution the end product is a manganous salt; in alkaline solution, manganese dioxide. Therefore it is a more powerful oxidizing agent in acid solution. U.S.P. and technical grades are sold. The U.S.P. grade contains 99-100 per cent on a dry basis. It is used as a general oxidizing agent, in the manufacture of dyes, as a disinfectant in medicine, and for bleaching. It is a standard oxidizing agent in the chemical laboratory.

Potassium bichromate, or **potassium dichromate,** $K_2Cr_2O_7$, is the red acid salt corresponding to the theoretical $KHCrO_4$, of which two molecules have united with the loss of a molecule of water. Potassium bichromate behaves like an acid salt although it lacks the hydrogen in its formula. It is moderately soluble in cold water but very soluble in hot. Adding regulated amounts of sulfuric acid to crude potassium chromate in aqueous solution forms the bichromate. It is also made from sodium bichromate by concentrating the solution with potassium chloride. Sodium chloride precipitates, and the bichromate is crystallized by further concentrating. In acid solution it is a powerful oxidizing agent. Sulfuric acid is usually added because hydrochloric acid is itself oxidized to chlorine. Potassium bichromate is put to many uses as an oxidizing agent, although the corresponding sodium compound is cheaper. The potassium compound is not deliquescent; the sodium compound is.

Potassium hypophosphite or **monopotassium hypophosphite,** KH_2PO_2, is very soluble in water and is soluble in alcohol. It is obtained by the reaction of calcium hypophosphite and potassium carbonate and is used in medicine.

Potassium silicate is an alkaline, water-soluble salt of somewhat indefinite composition sold for special purposes, such as coating lamp bulbs, where the sodium salt will not serve. It is furnished in lump form. Theoretically all of the sodium silicates except the orthosilicate could be paralleled with potassium salts but practically, demand for many of the latter does not exist.

Potassium cyanide, KCN, is extremely soluble in hot or cold water and is also soluble in alcohol or glycerine. When potassium carbonate and carbon are heated in a current of ammonia, potassium cyanide is produced. Potassium cyanide is extracted from the fusion with alcohol. It can also be obtained by fusion of calcium cyanamide with caustic potash. The salt gives an alkaline reaction in solution and is deliquescent. Its outstanding property is its extremely poisonous nature, since it is a salt of prussic acid. It was formerly used in electroplating and gold extraction as well as for other purposes, but has been largely replaced by the cheaper sodium cyanide.

Potassium ferrocyanide or **yellow potassium prussiate,** $K_4Fe(CN)_6,3H_2O$, is a nonpoisonous, yellow salt, very soluble in cold water and extremely soluble in hot. It is produced by heating nitrogenous matter, such as blood residues, with iron filings and potassium carbonate. The potassium cyanide and ferrous sulfide formed react to give potassium ferrocyanide. Sulfates, carbonates, chlorides and calcium salts may be present as impurities. It is used to make the ferricyanide, for making Prussian blue, ferric ferrocyanide, and in medicine and engraving. It is a mild reducing agent.

Potassium ferricyanide or **red potassium prussiate,** $K_3Fe(CN)_6$, is a nonpoisonous red salt, very soluble in water and slightly soluble in alcohol. It is made by oxidizing potassium ferrocyanide with chlorine. It is used in making pigments, blueprint paper, in etching liquid and in printing cotton fabric and dyeing wool. It is a mild oxidizing agent and used to some extent in synthetic organic chemistry for that purpose.

Potassium arsenite, or **potassium metarsenite,** $KAsO_2$, is a water-soluble salt slightly soluble in alcohol. It is prepared by solution of arsenious oxide in potassium hydroxide. The U.S.P. grade is sold as a solution for medicinal use, and contains the equivalent of 0.950-1.050 gram of arsenic trioxide per 100 cc. of solution.

CHAPTER VI

SODIUM AND POTASSIUM SALTS OF ORGANIC ACIDS

The commercial sodium salts of organic acids are rather limited in number. Their importance is minor only when compared with the sodium salts of inorganic acids. Potassium salts of organic acids are of less importance, with exceptions where the stability of the compounds dictates their use.

Sodium acetate, $NaC_2H_3O_2$, is very soluble in cold water, extremely soluble in hot water and moderately soluble in alcohol. The usual form is a trihydrate, $NaC_2H_3O_2,3H_2O$. It is made by reaction of acetic acid and soda ash and may also be produced from the crude pyroligneous acid from wood distillation, in which case the solution is concentrated to precipitate the salt and the crystalline mass separated by centrifuging. Another procedure is to treat calcium acetate with soda ash and sodium sulfate. The solution is filtered from calcium salts, the filtrate evaporated to dryness, the residue heated to about 250° C., dissolved in water and recrystallized.

The U.S.P. grade is the trihydrate, and when dried at 120° C. contains not less than 99 per cent of sodium acetate. Before drying the water content is 36-41 per cent. The commercial grades are anhydrous and what is called flake 60 per cent. The latter term means that it contains 60 per cent of the anhydrous salt. Uses are in the preparation of other acetates, in synthetic organic chemistry, in medicine, etc.

Potassium acetate, KO_2CCH_3, is a salt very soluble in alcohol and extremely soluble in water. It is formed by the reaction of acetic acid and potassium carbonate. Impurities such as chlorides, sulfates and heavy metals may be carried over from the crude potash unless a good grade is used. U.S.P. solid, containing not less than 99 per cent when dried to constant weight, and 50 per cent solutions are sold. The acetate is used in making crystal glass, as a dehydrating agent and in medicine.

Sodium oxalate, $Na_2C_2O_4$, is moderately soluble in cold water and about twice as soluble in hot. It is obtained by neutralizing oxalic acid with soda ash, filtering and recrystallizing. Carbonates, chlorides, sulfates, acid oxalate, iron and potassium may be present as impurities in the lower grades. Various qualities are sold. The salt is used in pyrotechnics and in textile and leather finishing. Its sale is controlled by the Caustic Poison Act, given in Appendix A.

Potassium oxalate, $K_2C_2O_4,H_2O$, is very soluble in water. Heating potassium formate or carbonate with a small quantity of oxalate and a slight excess of alkali produces the product, which is then crystallized. A pure crystalline, and a technical grade are sold. It is used as bleaching agent and in medicine. Its sale is controlled by the Caustic Poison Act, given in Appendix A.

Potassium binoxalate or **potassium acid oxalate,** KHC_2O_4, forms deliquescent crystals very soluble in water. It is obtained by mixing a solution of normal potassium oxalate with oxalic acid, from which the acid salt separates on evaporation. It is used for bleaching straw, cleaning metals and wood, in photography, and to remove ink stains. Its sale is controlled by the Caustic Poison Act, given in Appendix A.

Potassium titanium oxalate, $TiO(KC_2O_4)_2,2H_2O$, exists as greenish, water-soluble crystals. It results from treating titanium hydroxide with oxalic acid and potassium hydroxide, and is used as a mordant in dyeing leather and cotton. Its sale is controlled by the Caustic Poison Act, given in Appendix A.

Sodium citrate, $2Na_3C_6H_5O_7,11H_2O$, is extremely soluble in hot or cold water and slightly soluble in alcohol. It is prepared from calcium citrate by treatment with sodium sulfate, filtration and crystallization from the filtrate. Calcium sulfate may be present as an impurity. Since practically the only use is in medicine and food products, usually only granular U.S.P. VIII and X grades are quoted. U.S.P. XI gives the dihydrate, containing 10-13 per cent of water, and 99 per cent of the anhydrous salt on a dry basis.

Potassium citrate, $K_3C_6H_5O_7,H_2O$, is very soluble in water and is formed by the reaction of citric acid with potassium carbonate. It is used in medicine. The usual quoted grade is U.S.P., which contains 3-6 per cent of moisture and not over 1 per cent of other impurities.

Potassium bitartrate, potassium acid tartrate, or **cream of tartar,** $KHC_4H_4O_6$, is slightly soluble in cold water, but moderately soluble in hot. It is obtained as crude *argols*, which are the lees deposited in wine vats. Argols are sold as 75-85 per cent potassium bitartrate but are quoted on a 100 per cent basis. The salt is leached from these with water, clarified and recrystallized. The U.S.P. standard requires not less than 99.5 per cent purity when dried at 100° C. The purified or U.S.P. cream of tartar is used as the acid ingredient of baking powder, for preparation of tartaric acid and practically all other tartrates, and in medicine.

Sodium potassium tartrate, potassium sodium tartrate, or **Rochelle salt,** $KNaC_4H_4O_6{,}4H_2O$, is very soluble in cold water and extremely soluble in hot. By saturating an aqueous solution of potassium acid tartrate with soda ash and concentrating, the salt is crystallized. The U.S.P. grade contains 21-26 per cent of water, corresponding to the tetrahydrate, and not more than 1 per cent of other impurities. Both powdered and crystalline forms are sold, largely for medicinal use, and to serve as a reducing agent, as in silvering mirrors.

Sodium soap or **soda soap** is a term applied to the most widely used organic salts of sodium. The general term **soap** usually refers to sodium soap. Commercial soap is seldom a chemical individual, but is a mixture of the sodium salts of several fatty acids, one of which may predominate. **Hard soap** or tallow soap sold for laundry use is largely **sodium stearate,** $NaO_2C(CH_2)_{16}CH_3$. This compound is also made in pure form by the reaction of purified stearic acid with caustic soda. It is sold under the name of sodium stearate in lump and powder forms of U.S.P. and less pure grades, for use in medicinal products and in cosmetics. The U.S.P. grade of hard soap is a neutral white soap containing no heavy metal soap and no added alkaline salts as builders. A so-called **neutral soap** usually contains not more than 0.05 per cent of free caustic alkali. A small amount of free alkali is desirable in order to avoid the formation of free fatty acids, which turn rancid rather easily. **Tallow chip soap** contains small proportions of fatty acid salts other than sodium stearate. It is sold with a soap content of 88-92 per cent, the balance being largely water.

Frequently, although not always, white toilet soaps contain 80-90 per cent of tallow soap or its equivalent, and 10-20 per cent of coconut-oil soap or its equivalent, in terms of anhydrous soap content. Coconut oil contains a high proportion of lauric acid as the glyceride. This is converted to sodium laurate, which helps to produce better lather and greater solubility of the soap at lower temperatures. The sodium salts of fatty acids present in liquid oils are also used for this purpose, such as **sodium oleate,** $NaO_2C(CH_2)_7CH:CH(CH_2)_7CH_3$. **Sodium palmitate,** $NaO_2C(CH_2)_{14}CH_3$, is intermediate in properties between the oleate and stearate. Such natural oils as corn, olive, cottonseed, etc., contain a large proportion of oleic acid glycerides. Palmitic acid soaps are derived mainly from palm oil. Natural oils and fats always contain a mixture of glycerides. In speaking of both glycerides and soap, it is rather common practice to describe them in terms of their fatty acid content, although it should be understood that the free fatty acids do not exist as such in either case.

The manufacture of soap is quite simple. The natural fat or oil mixture, which contains glycerides of fatty acids, is saponified or caused to react with caustic soda. Soap and glycerine are produced. The glycerine is recovered by salting out the soap from the excess lye layer containing the glycerine, in the "boiled" process, but not in the "half-boiled" nor in the "cold" process of saponification. Soap made by the latter two procedures therefore contains the glycerine and all other impurities originally present in the materials used. Processing of the soap to form cakes or chips and to incorporate perfume or other ingredients, is a matter of varied mechanical detail. When the natural fat has first been split into fatty acids and glycerine and the glycerine recovered, the fatty acids alone react rapidly with caustic soda to form soap. The methods for setting free the fatty acids usually causes them to darken, so that the appearance of soap made from them may be less desirable than that of soap made by direct saponification of natural fats.

Soap reaches the public in the form of cakes, chips, flakes, beads, etc. White bars usually are about 65 per cent soap and the balance water, but cake toilet soaps have usually been milled and contain only 8-12 per cent of water. Many soap products contain added builders such as soda ash, sodium silicate, borax or other alkaline salts, in addition to natural impurities. Soap which has been salted out after the boiling process contains some sodium chloride. Only very small amounts of free caustic soda are allowed to remain in the product, because of the irritating effect of caustic alkali on the skin. Yellow bar soaps usually contain very substantial amounts of rosin soap, sodium abietate, and an abnormally high water content. Soap is used as a general detergent.

Castile soap was originally made by the cold saponification of a good grade of olive oil with less than the equivalent amount of caustic soda, giving a superfatted soap, one containing an excess of unsaponified fat or of some fatty ingredient. Other fats are now added to the olive oil as a rule, and legally no olive oil need be used. It is still often made by the cold process or as a half-boiled soap, which means that all of the impurities present in the raw materials remain in the soap. Much however is boiled the same as any soap and the glycerine recovered. While white when fresh, Castile soap made by the cold process usually darkens on exposure to air and light, and develops a rancid odor. Aside from lathering in cold or tepid water, the virtues on which the reputation of Castile soap was built are largely present in other superfatted soaps. If made from oleic-acid oils, any superfatted soap is the commercial equivalent of Castile soap. Castile soap is quoted as **olive oil castile** in bar or powdered form. **Olive oil foot soap** in bars has a 68-70 per cent soap content. **Powdered white neutral soap** is also sold at a price much under powdered Castile, but is used for many of the same purposes. This should not be confused with **soap powder,** which is a crystallized mixture of soap with hydrated sodium carbonate, containing from 30 per cent of soap down to as little as 2 per cent. Soap powder is used for rough cleaning.

Mottled soap is a low-grade soda soap originally mottled because of incomplete mixing or use of impure alkali, but now intentionally produced of a mottled appearance from red or blue and white soap. It is largely an export product.

Sodium abietate, $NaO_2CC_{19}H_{29}$, is the water-soluble soap resulting from the reaction of caustic soda with abietic acid, or commonly by the saponification of rosin, which is the anhydride of abietic acid, with caustic soda. The market for the yellow to brown substance is mostly for the manufacture of heavy metal abietates, and as a paper sizing. Sodium abietate is present in substantial quantities in brown or yellow soaps, where it serves to increase lathering power.

Sodium ricinoleate, $NaO_2C(CH_2)_7CH:CHCH_2(OH)CH(CH_2)_5CH_3$, is the corresponding soap of ricinoleic acid, present in large proportion in castor oil. It is useful mainly as an emulsifying agent.

Sodium sulforicinoleate is a water-soluble soap resulting from the sulfonation and subsequent saponification of castor oil. It is of indefinite composition because of incomplete sulfonation. Substantial amounts of sodium sulfate and other extraneous materials are present, as well as sodium ricinoleate from the saponification of unsulfonated castor oil, which contains a large proportion of glycerides of ricinoleic acid. It is sold in liquid form and used as an emulsifying and wetting agent.

Sodium alkyl sulfates such as **sodium lauryl sulfate,** $NaSO_3C_{11}H_{23}$, are not sold under their chemical names but under varied trade names, usually mixed with sodium sulfate. Similarly a series of sodium salts of organic sulfonates are sold. Both types are of importance as wetting agents in many industries, particularly in the textile field. Some have the properties of soap without forming insoluble calcium and magnesium salts in hard water.

Potassium soaps differ from sodium soaps in being soft. They are often referred to as paste soaps. The corresponding salts exist as **potassium stearate, potassium oleate, potassium palmitate, potassium abietate,** and **potassium ricinoleate.** Practically, most soft soaps are either mainly potassium oleate or potassium soap made from coconut oil. While definite grades of potassium soaps are seldom offered as such, the paste soft soaps vary between 30 and 60 per cent of actual soap content, the balance being water and glycerine.

Green soap is a U.S.P. product. It is about a 40 per cent mixed soda and potash soap, with the soda soap predominating, made from linseed oil. It may also be entirely a potash soap. Excess alkali is intentionally present. Green soap is used as a medicinal agent. When 65 grams of the soap are mixed with 2 cc. of oil of lavender and diluted to 100 cc. with alcohol this constitutes **tincture of green soap.** The liquid must be filtered and again made up to volume with alcohol.

Sodium glycerophosphate, $Na_2PO_3C_3H_7O_3,H_2O$, is a water-soluble organic phosphate obtained by neutralizing glycerophosphoric acid with soda ash. It is an N.F. rather than a U.S.P. material, and is used largely in medicine. It is available in powder form as well as in 50 and 75 per cent solutions.

Potassium glycerophosphate, $K_2PO_3C_3H_7O_3,(H_2O)_n$, is a colorless to yellow doughy material extremely soluble in water. Warming glycerine and metaphosphoric acid together, neutralizing with potassium carbonate and concentrating, gives this salt. The salt and a 75 per cent solution are both sold for use in the manufacture of medicinal preparations.

Sodium cacodylate, $Na(CH_3)_2AsO_2,3H_2O$, is a hydrated organic derivative of arsenic, very soluble in water and moderately soluble in alcohol. Made by the usual methods for organic-salt synthesis, the product is largely of U.S.P. grade, which contains 72-75 per cent of the anhydrous salt. It is expensive and its use as a medicinal is limited.

Potassium ethyldithiocarbonate, potassium xanthate, potassium xanthogenate, or **potassium ethylxanthogenate,** $KS_2COC_2H_5$, is prepared by reaction of potassium ethylate and carbon disulfide and is sold as colorless or light yellow crystals, soluble in water and alcohol. It is used for medicinal purposes and as a fungicide for treatment of the soil.

Sodium benzoate or **benzoate of soda,** $NaO_2CC_6H_5$, is very soluble in hot or cold water and moderately soluble in alcohol. It is made by neutralizing benzoic acid with sodium bicarbonate solution and crystallizing. It gives a slightly alkaline reaction in aqueous solution due to hydrolysis. Grades are U.S.P., which contains not more than 1 per cent of impurities on a dry basis, and technical. The purity of the latter approaches that of the U.S.P. grade. The major use is as a preservative for prevention of bacterial growth. Its inclusion in food products must be declared on the label. The usual amount as a preservative is 0.1 per cent but this is only effective at a proper degree of acidity.

Sodium salicylate, $NaO_2CC_6H_4OH$, is a salt very soluble in water, obtained by heating sodium phenolate with carbon dioxide under pressure. The U.S.P. grade contains not more than 0.5 per cent of impurities on a dry basis. It is used in some countries as a preservative in much the same way that sodium benzoate is used, although it is more expensive. Its use in food products is illegal in the United States, even if declared on the label. It is also used in medicine.

Sodium metanilate, $NaSO_3C_6H_4NH_2$, is the *meta* sodium sulfonate of aniline, sold either as a solid or in 20 per cent aqueous solution. It is prepared by neutralization of metanilic acid, which is an article of commerce, and is used in the manufacture of synthetic dyestuffs and drugs.

Sodium sulfanilate, $NaSO_3C_6H_4NH_2,2H_2O$, is the *para* sodium sulfonate produced by neutralizing sulfanilic acid, which is also a chemical of commerce. The white crystalline material is soluble in water and is used for the synthesis of dyes, intermediates and drugs. It is isomeric with sodium metanilate but much less expensive.

Sodium sulfocarbolate or **sodium phenolsulfonate,** $NaSO_3C_6H_4OH,2H_2O$, is a water-soluble derivative of phenol or carbolic acid, prepared by sulfonating phenol and neutralizing with caustic soda. It is used for its antiseptic properties.

Sodium picramate, $NaOC_6H_2(NO_2)_2(NH_2)$, is the yellow, water-soluble salt obtained by neutralizing picramic acid with caustic soda. It is used in dye manufacture.

Sodium *ortho*-chlorotoluene-*para*-sulfonate, $NaSO_3C_6H_3(CH_3)Cl$, is the product of sulfonation of *ortho*-chlorotoluene, neutralized to form the sodium salt. It is soluble in water and organic solvents and used in the synthesis of dyes, intermediates and drugs.

Potassium guaiacol sulfonate, $KSO_3C_6H_3(OH)(OCH_3)OH$, is moderately water-soluble and results from the sulfonation of guaiacol and neutralization with potassium hydroxide or carbonate. It is sold in powder form for medicinal use.

Sodium naphthionate or **sodium** *alpha*-**naphthylamine sulfonate,** $NaSO_3C_{10}H_6NH_2,4H_2O$, is a water-soluble salt. It is obtained by sulfonating *alpha*-naphthylamine by means of concentrated sulfuric acid. After the reaction is complete and the product has cooled down, it is neutralized with caustic soda, filtered, and the filtrate concentrated to crystallization. It is sold as crystals or paste for use in synthetic organic chemistry, and for the detection of small amounts of nitrous acid.

Sodium naphthenate is the mixture of water-soluble compounds of indefinite composition resulting from the neutralization of complex naphthenic acids derived from petroleum. Varied grades are sold as solutions in petroleum, often containing relatively minor amounts of sodium naphthenate but quoted on the basis of their actual content. The uses are varied but largely relate to emulsification or use as wetting agents.

Schaeffer's salt, $NaSO_3C_{10}H_6OH$, is the water-soluble sodium salt of **2-naphthol 6-sulfonic acid** and is prepared by the sulfonation of *beta*-naphthol, purification and neutralization. It is used for the preparation of dyes and intermediates.

G salt, $(NaSO_3)_2C_{10}H_5OH$, is the sodium salt of **2-naphthol-6,-8-disulfonic acid,** prepared by the more complete sulfonation of *beta*-naphthol than for Schaeffer's salt, followed by neutralization. The white needles are soluble in water and are used in the manufacture of intermediates and azo dyes. A paste form is also sold.

R salt, $(NaSO_3)_2C_{10}H_5OH$, is the disodium salt of **2-naphthol-3,6-disulfonic acid** prepared from the proper sulfonation of *beta*-naphthol, followed by neutralization with alkali. It is used in the preparation of dyes and intermediates.

Sodium alginate is a salt of alginic acid, derived from seaweed, which dissolves or disperses in water. The composition is indefinite. It is used as an emulsifying agent, and in boiler compounds.

Vegetable potash is a distillery waste by-product from the molasses mash used for alcohol production. It is relatively low in potash and is sold as a bulk product for use in mixed fertilizers. It is sold in varied forms, including the ash, and the ash treated with sulfuric acid to convert the compounds to sulfates.

CHAPTER VII

AMMONIUM AND LITHIUM COMPOUNDS

Ammonia, NH_3, presents the unusual case of a chemical compound of nitrogen and hydrogen which acts as an element. It is a gas which dissolves in water to give an alkaline solution, ammonium hydroxide, discussed under "Alkalies," where the manufacture of ammonia is also covered. The solution reacts with acids to form a series of salts, comparable to those of the alkalies, many of which are of industrial importance. In these the ammonium radical, NH_4, is the equivalent of Na in sodium salts. Ammonium salts are often incorrectly termed ammonia salts, just as the aqueous solution is often referred to as ammonia. Nearly all of the salts are white and water-soluble, and have other properties closely related to those of corresponding sodium or potassium compounds.

Ammonium sulfate, $(NH_4)_2SO_4$, is an extremely water-soluble salt which is an important form of crude fixed ammonia. By distillation of the crude washings of coal gas mixed with lime, ammonia is liberated and absorbed in sulfuric acid. Lower grades are off-color due to traces of tars present. While at one time large amounts were imported, the material has become an export product. Its major use is in fertilizers. A typical minor use is as a flux for soldering and for the galvanizing of iron.

Ammonium persulfate, $(NH_4)_2S_2O_8$, is a very soluble salt obtained by electrolyzing a concentrated solution of ammonium sulfate or bisulfate. It is used as an oxidizing and bleaching agent in oxidizing copper and in bleaching oils. It is also used for the manufacture of potassium persulfate.

Ammonium sulfide is a very soluble salt which can be obtained as a solid only with great difficulty. The theoretical composition is $(NH_4)_2S$. A polysulfide, $(NH_4)_2S_5$, also exists. The commerical product is normally a solution of **ammonium hydrosulfide,** NH_4HS. This is prepared by saturation of ammonium hydroxide with hydrogen sulfide gas. Uses are for producing sulfide finishes on metals such as copper, brass and silver, often known as oxidized finishes. It is also used to denitrate nitrocellulose products.

Ammonium chloride or **sal ammoniac,** NH_4Cl, is very soluble in water, even when cold, and slightly soluble in alcohol. It is produced by methods similar to those described for ammonium sulfate, the ammonia being absorbed in hydrochloric acid. Ammonium chloride is a by-product of the ammonia-soda process and may also be obtained from metal pickling liquors containing ferrous chloride, by neutralization with ammonia. A U.S.P. grade is furnished in granular form, containing not more than 0.5 per cent of impurities, on a dry basis. The term sal ammoniac is usually applied to the crude grade which is off-color. White, granular, technical material is often so designated. Numerous applications include as soldering flux, as electrolyte in dry cells, in fertilizers, in textile printing and in medicine.

Ammonium bromide, NH_4Br, is very soluble in cold water and extremely soluble in hot. It also dissolves in alcohol and ether. It is prepared by the reaction of bromine and ammonium hydroxide. The U.S.P. grade contains not more than 1 per cent of impurities, on a dry basis. Ammonium bromide is used for its bromide content in medicine, and as a precipitating agent for silver salts in photography.

Ammonium iodide, NH_4I, is extremely soluble in water and very soluble in alcohol. It is prepared by neutralizing hydriodic acid with ammonium hydroxide, and is used in medicine and in the photographic industry.

Ammonium fluoride, NH_4F, is very soluble in cold water, is decomposed by hot water and is slightly soluble in alcohol. It is manufactured by fully neutralizing hydrofluoric acid with ammonium hydroxide. Ammonium fluoride is used as a strong antiseptic and preservative, as an etching agent for glass, and in treatment of soils.

Ammonium bifluoride or **ammonium acid fluoride,** NH_4HF_2, is a very soluble salt obtained by half-neutralizing hydrofluoric acid with ammonium hydroxide, and crystallizing. It is used for etching glass, as a sterilizing agent and as a textile sour.

Ammonium fluosilicate or **ammonium silicofluoride,** $(NH_4)_2SiF_6$, is a very soluble salt prepared by methods analagous to those described for sodium silicofluoride. It is used for similar purposes to those for the latter compound, and has a greater solubility in water.

Ammonium perchlorate, NH_4ClO_4, is the very soluble salt obtained by neutralizing perchloric acid with ammonium hydroxide. It is a very strong oxidizing agent and is used in explosives and pyrotechnics.

Ammonium nitrate, NH_4NO_3, is extremely soluble in water and moderately soluble in alcohol. It is produced by neutralizing nitric acid with ammonium hydroxide. The great solubility of the salt and its small molecular weight recommend it for lowering the freezing point of water. It decomposes on heating, producing a large volume of gases. These two properties make the technical product useful in freezing mixtures, and in explosives, respectively. The high nitrogen content makes it of value in fertilizers.

Ammonium phosphate is a general rather than a specific term. **Monoammonium phosphate, primary ammonium phosphate,** or **monobasic ammonium phosphate,** $(NH_4)H_2PO_4$, is very soluble in cold water and extremely soluble in hot. It results from neutralizing phosphoric acid with one-third its equivalent of ammonium hydroxide. A pure grade is sold for use in medicine. It is used to some extent as a fireproofing agent for textiles. A fertilizer grade combines in one salt both fixed nitrogen and phosphate, and is quoted on a basis of 11 per cent nitrogen and 48 per cent phosphorus pentoxide. **Diammonium phosphate, secondary ammonium phosphate** or **dibasic ammonium phosphate,** $(NH_4)_2HPO_4$, is very soluble in water. It is produced by neutralizing phosphoric acid with two-thirds the equivalent amount of ammonium hydroxide. Monoammonium phosphate is apt to be present. An N.F. V grade is used in medicinals. The technical grade is probably the best known textile-fireproofing agent, although it has the disadvantage of water solubility. It is also a fertilizer material. The theoretical **triammonium phosphate,** $(NH_4)_3PO_4$, can be produced, but on exposure to air gives off ammonia to form the diammonium compound. It is therefore relatively unimportant.

Ammonium hypophosphite, $NH_4H_2PO_2$, is an alcohol- and water-soluble salt obtained by neutralizing hypophosphorous acid with ammonium hydroxide. It is used in medicine and as a reducing agent.

Ammonium carbonate, sometimes called **ammonium crystals,** is a salt which is very soluble in water. The theoretical composition is $(NH_4)_2CO_3$. It is obtained as the **sesquicarbonate** or commercial form by heating together ammonium sulfate and chalk, condensing and resubliming the vapors. The commercial product is a mixture of ammonium bicarbonate, NH_4HCO_3, and ammonium carbamate, $NH_4NH_2CO_2$, containing about 31 per cent of ammonia, 57 per cent of carbon dioxide and 12 per cent of combined water. Absorption of carbon dioxide tends to revert the carbamate to the bicarbonate. It is more of theoretical than practical interest that the carbonate results from saturation of a concentrated solution of the bicarbonate with ammonia, since this has a very definite tension of ammonia when exposed to air, and therefore decomposes readily. The mixed bicarbonate-carbamate is sold in U.S.P. lump, cube and powder forms for medicinal use, a grade which yields 30-32 per cent of anhydrous ammonia. Technical grades are used for various purposes as in smelling salts, for the manufacture of special ammonium salts, in fire-extinguishing compounds, in rubber accelerators, etc.

Ammonium bicarbonate, ammonium acid carbonate or **ammonium hydrogen carbonate,** NH_4HCO_3, is very soluble in water. It results from saturating a solution of ammonium carbonate with carbon dioxide. The bicarbonate is unstable and readily loses carbon dioxide. Ammonium carbonate may therefore be present as an impurity. The acid salt is used in medicine to some extent. Since it contains over 50 per cent of carbon dioxide it is an ingredient of some fire-extinguishing compounds.

Ammonium bichromate or **ammonium dichromate,** $(NH_4)_2Cr_2O_7$, is an orange salt, very soluble in water and soluble in alcohol. It is prepared by neutralizing chromic acid with ammonium hydroxide, and is used for many of the same purposes as sodium or potassium bichromate, when there are special reasons justifying the higher price of the ammonium salt. It decomposes on heating and therefore has some use in pyrotechnics.

Ammonium borate, ammonium biborate or **ammonium acid tetraborate,** $NH_4HB_4O_7,3H_2O$, is a water-soluble salt obtained by the reaction of boric acid and ammonium hydroxide. Structurally it is an acid salt, although its aqueous solution is slightly alkaline. Commercially, several different compositions have been sold. It is used in medicine, as a fire-proofing agent and in condenser electrolytes.

Ammonium thiocyanate, ammonium sulfocyanide, ammonium sulfocyanate or **ammonium rhodanide,** NH_4SCN, is deliquescent, extremely soluble in water, and soluble in alcohol. It is prepared by reaction of ammonium cyanide and sulfur, and is used for the preparation of related compounds such as thiourea, in photography, and in the dyeing and printing of textiles.

Ammonium oxalate, $(NH_4)_2C_2O_4,H_2O$, is very soluble in hot water and moderately soluble in cold. It is obtained by the reaction of oxalic acid with ammonium hydroxide. Ammonium oxalate is sold in crystalline and powdered form for the manufacture of special explosives and for removal of corrosion from metals.

Ammonium acetate, $NH_4O_2CCH_3$, is the extremely soluble hygroscopic salt obtained by the reaction of strong acetic acid and ammonia gas. It is also soluble in alcohol. A U.S.P. solution contains 6.5-7.5 grams of the salt per 100 cc. of solution. It is used in dyeing and as a medicinal.

Ammonium lactate, $NH_4O_2CCHOHCH_3$, is a clear, syrupy, hygroscopic liquid, colorless or more often slightly yellow, with a slight odor of ammonia. When warmed it loses its ammonia content. It is miscible with water or alcohol. Uses are in electroplating and in leather tanning and finishing.

Ammonium citrate, $(NH_4)_3C_6H_5O_7$, is water-soluble and slightly alcohol-soluble. It is produced by neutralizing citric acid with ammonium hydroxide and is very deliquescent. Uses are in rustproofing and in cotton printing.

Ammonium soaps or **ammonia soaps** result from the reaction of the appropriate fatty acid with ammonium hydroxide. Unlike sodium and potassium soaps these are not sold as detergents for general use. They have an appreciable vapor pressure of ammonia and therefore on continued exposure will decompose, leaving the fatty acid as a residue. These soaps are often present as minor ingredients in other products. Several individual ammonium soaps are sold as such, particularly for use in the manufacture of toilet preparations and emulsions. All are made by neutralization of the corresponding acid with ammonia. Quotations for ammonia soaps are substantially higher than the combined cost of the fatty acid and ammonium hydroxide. In many cases the fatty acid and ammonium hydroxide can be incorporated individually in the product during manufacture, in preference to use of the preformed soap.

Ammonium laurate, $NH_4O_2CC_{11}H_{23}$, is a tan-colored paste, very soluble in water and soluble in alcohol or ether. It is used in cosmetic products and as an emulsifying agent.

Ammonium oleate, $NH_4O_2C(CH_2)_7CH{:}CH(CH_2)_7CH_3$, is similar in properties and uses to the laurate. The general term ammonia soap, usually refers to the oleate. **Ammonium linoleate,** $NH_4O_2CC_{17}H_{31}$, is sold as an anhydrous 80 per cent product and is used similarly to the laurate. **Ammonium ricinoleate,** $NH_4O_2CC_{17}H_{32}OH$, is white and similar in uses to the laurate.

Ammonium stearate, $NH_4O_2C(CH_2)_{16}CH_3$, is an ammonium soap, a white or yellow to tan mass or powder. Both anhydrous solid and paste forms are sold. It is used as an emulsifying agent, as a waterproofing agent in concrete, and in the preparation of other stearates.

Ammonium naphthenate is the indefinite pasty mixture formed by neutralizing naphthenic acids, obtained as a mixture from petroleum, with ammonium hydroxide. The material is used in much the same way as ammonium soaps of fatty acids.

Ammonium benzoate, $NH_4O_2CC_6H_5$, is a water-, alcohol- and glycerine-soluble salt of benzoic acid, prepared by neutralizing benzoic acid with ammonium hydroxide. The U.S.P. salt contains not more than 2 per cent of impurities after drying over sulfuric acid. It is sold as a powder for use as a preservative.

Ammonium salicylate, $NH_4O_2CC_6H_4OH$, is a very soluble salt obtained by neutralizing salicylic acid with ammonium hydroxide. The U.S.P. grade is similar to that of ammonium benzoate. Ammonium salicylate is used in medicine and as a preservative.

Lithium, Li, is one of the alkali metals closely related to sodium and potassium, but is less active than these. It is found in the minerals petalite and lepidolite. Some lithium salts occur in the soil and in mineral springs. Few compounds are common in commerce. The relatively high price of the compounds is one limitation on their use. In general lithium salts are white and water-soluble.

Lithium carbonate, Li_2CO_3, is relatively insoluble in water. It is precipitated from an aqueous solution of lithium chloride by adding sodium carbonate. Some lithium chloride and sodium carbonate may be carried down with the precipitate. It is used in medicine and in artificial mineral waters.

Lithium chloride, LiCl, is very soluble in cold water and exceedingly soluble in hot. It is also soluble in alcohol and ether. The compound is produced by solution of lithium carbonate or lithium hydroxide in hydrochloric acid and crystallization. It is used in mineral waters and pharmaceuticals. Since lithium gives a red color in a flame, the salt is used in pyrotechnics.

Lithium bromide, LiBr, is extremely soluble in water. It results from the reaction of lithium carbonate or lithium hydroxide with hydrobromic acid and is used in medicine and in photography.

Lithium iodide, LiI, is similar to the bromide in properties. The method of preparation is the same except that hydriodic acid replaces hydrobromic acid. The uses are similar.

Lithium fluoride, LiF, is only slightly soluble in water. It results from the treatment of lithium carbonate with hydrofluoric acid. The limited use of this material is largely in the ceramic industry.

Lithium citrate, $Li_3C_6H_5O_7,4H_2O$, exists as deliquescent crystals, very soluble in water and also soluble in alcohol and ether. The aqueous solution is alkaline. It is prepared by the reaction of citric acid with lithium carbonate and is used in medicine.

CHAPTER VIII

CALCIUM COMPOUNDS

Since calcium compounds are one of the major ingredients of the earth's crust numerous relatively low-priced derivatives are important in the chemical industry. In general the compounds in pure form are white.

Calcium, Ca, is a silver-white metal which reacts with water much as sodium does but less actively. It is prepared by electrolyzing fused calcium chloride. Its oxide, lime, CaO, is the source of an important alkali, calcium hydroxide. From this is derived the popular terminology for calcium compounds of **lime compounds** or **lime salts.**

Calcium carbonate, $CaCO_3$, appears on the market in many forms and depends on its relative insolubility in water for many of its uses. In finely divided form it renders water distinctly alkaline. It is soluble in acids because it reacts to form the corresponding calcium salt and liberate carbon dioxide. This reaction proceeds more rapidly if the resulting salt is a soluble one, than if it is relatively insoluble. Many of the forms of calcium carbonate are sold in massive units. Limestone used for building purposes is a naturally occurring material. In broken pieces it is used as a metallurgical flux. Some limestone is relatively low in calcium carbonate, **dolomitic limestone** containing roughly 60 per cent of calcium carbonate and 40 per cent of magnesium carbonate. For many purposes the magnesium-salt content is equivalent to the calcium salt. **Marble** is a crystalline form, often beautifully colored by traces of impurities. **Chalk** as a mineral, is another form of naturally occurring calcium carbonate. These natural forms of calcium carbonate merely have to be quarried.

Marble chips, recovered in the quarrying of marble slabs and blocks, are sold of various sizes. They are used as fillers in many types of artificial stone and as low-cost bulk-producers. They are sometimes used for neutralization of acids, a convenient method which requires little attention, because an excess of the neutralizing agent will not dissolve. This use is in competition with lime and with the soluble alkalies.

Marble flour or **marble dust** is similar in nature to the chips but more finely ground. Since it is a low cost product and since marble is widely distributed, local supplies are normally used. It serves the same purposes as the chips. Various degrees of fineness are obtainable. Some grades are used as abrasives in paste hand soaps.

Whiting is ground natural calcium carbonate. Usually it is about a 98 per cent grade, the balance being natural contaminants such as silica, iron, aluminum and magnesium. Whiting of various grades, including those given below, is used as an inexpensive filler in rubber and various other products, as a pigment extender in paints, especially of the water type, and as an abrasive for varied purposes. Such an **extender** for pigments is inexpensive and differs from a true pigment both in particle size and, what is more important, index of refraction. This index differs substantially from that of the vehicle in the case of a true pigment but differs much less for an extender. The result of small difference in the index of refraction is low hiding power.

Limestone whiting is ground limestone, a grade not as soft as chalk whiting. Typical grades by particle size of the dry-ground and air-floated material are 93 per cent through 200 mesh, 95-98 per cent through 200 mesh, 99 per cent through 200 mesh and 99 per cent through 300 mesh. The wet-ground, water-floated material is sold as gilders, gilders extra and putty grades. Many other special.grades are prepared and sold.

Chalk whiting means the crude material from natural chalk cliffs which has been ground, washed and dried. Commercial dry-ground is the coarsest grade. Wet-ground is somewhat finer. Gilders-bolted is the next grade and extra bolted is even finer. **Paris white** is the finest grade and is English cliffstone.

Precipitated whiting is obtained by chemical reaction. This may be made with soluble calcium and carbonate salts, such as calcium chloride and sodium carbonate, or with carbon dioxide and limewater.

Precipitated calcium carbonate or **precipitated chalk** is a better quality of material, made by the reactions indicated for precipitated whiting. It is of heavy, light, and extra light grades, referring to bulk density. The U.S.P. grade contains not more than 2 per cent of impurities on a dry basis. Aside from uses similar to those outlined for whiting, it is an ingredient of cosmetics and an abrasive in tooth paste.

Prepared chalk or **dropped chalk** is a U.S.P. product. It is natural calcium carbonate freed from impurities by washing, and when dried to constant weight at 200° contains not less than 97 per cent of calcium carbonate. Varied uses include treatment of burns, administration as an antiacid, etc.

Putty is a flexible mixture of whiting and linseed oil used by glaziers for holding glass in place. It is also used as a crack filler and for some miscellaneous applications. Putty sets by drying of the oil, due to oxidation. Various grades sold are commercial, raw linseed, refined linseed and standard. Some putty has pigment added to give increased whiteness and opacity, but this is not standard practice.

Roasting calcium carbonate gives **calcium oxide, lime,** or **quicklime,** CaO. The decomposition is promoted by removing the carbon dioxide produced, by means of a strong current of air. It reacts with water to produce hydrated lime which is slightly soluble. The rate of this reaction is highly variable as a result of different conditions of burning and varying compositions. Commercial forms of lime are lump or pebble, ground, fine-ground, and hydrated. As the hydrate it is an alkali, which has already been discussed under that subject. Lime is used as a general source of calcium, in soil treatment, in plaster, in rubber, in the manufacture of many chemicals, as a clarifying agent when suspended in water, and for many purposes as the hydrate.

Calcium sulfate is another compound of calcium nearly insoluble in water. It occurs in nature as the dihydrate, $CaSO_4.2H_2O$, known as **gypsum,** deposits of which are widely distributed. It may have varying colors due to natural impurities. Calcium sulfate occurs to a lesser extent in the anhydrous form as **anhydrite,** $CaSO_4$. The term gypsum is rather loosely used in the trade, often referring to calcium sulfate in any form. When calcined to the hemihydrate, $CaSO_4.\frac{1}{2}H_2O$, it is known as **plaster of Paris.** In a fine grade this is sold as **Dental plaster.** Since plaster of Paris sets rapidly on mixing with water, organic retarders such as glues or casein are added. In that form it is one of the most common building plasters, since, mixed with sand, it sets in a few hours by rehydration to gypsum. Other forms are **Keene's cement** and **stucco gypsum.** Plaster of Paris and its modified forms are used for many types of casting, coating, etc. Ground gypsum is an inexpensive filler in many products. It competes with chalk. Precipitated forms resulting as by-products in other industries are used as mild polishing agents, as in tooth paste. **Terra alba** is a form sold in domestic and imported grades.

Satin white is a grade of white pigment containing calcium sulfate, lime and aluminum hydroxide. It is made by the precipitation of aluminum sulfate with lime. This results in the formation of calcium sulfate and aluminum hydroxide, but excess lime is usually present. Calcium aluminate may also be present. It is sometimes called **satin spar** but that term is more correctly applied to varieties of calcium carbonate and of calcium sulfate which have a satiny luster. Various uses as pigment include the surfacing of paper, as a base for lakes, in paint manufacture, as a filler in various compositions, etc. It is inexpensive as compared with pigments, but expensive as compared with pigment extenders.

Calcium sulfide, CaS, is nearly insoluble in water but soluble in acids. It results from heating the sulfate with charcoal or coke, or by heating lime in a current of hydrogen sulfide. The aqueous solution hydrolyzes to give an alkaline reaction and the odor of escaping hydrogen sulfide gas. **Crude calcium sulfide** or **sulfurated lime** contains some unreduced sulfate. It is sold as a 75 per cent grade passing through 100 mesh, and as an 83-85 per cent grade. The combination of alkali and sulfide in water rapidly attacks the hair on animal skins and is the basis of its use both as a depilatory in the tanning industry and in cosmetics. **Luminous sulfide,** 120 mesh, is another commercial form. This is used in luminous paint, as it will glow in the dark after previous exposure to sunlight. It owes this property to the presence of impurities such as bismuth, vanadium and rare earths.

Lime-sulfur is a yellow to grey complex mixture formed on heating lime-water with flowers of sulfur. It contains multiple sulfides such as CaS_2 and CaS_5 and some sulfate. It is sold dry, or more commonly as a slurry, and is used as a fungicide.

Calcium chloride, $CaCl_2$, is an extremely soluble salt of calcium. It forms many hydrates of which $CaCl_2{,}2H_2O$ and $CaCl_2{,}6H_2O$ are typical. It occurs in natural waters in many places and is obtained commercially as a by-product in many industries, as in the Solvay process for making sodium carbonate. Much is wasted for lack of a market but the expense of recovery maintains the price at a surprisingly high level. While the anhydrous salt can be made by heating the hydrate in a stream of hydrogen chloride, it is unimportant. Commercial grades are flake, 77-80 per cent, and solid, 73-75 per cent. A 40 per cent solution is also sold. The U.S.P. salt is the dihydrate, containing 75-85 per cent of anhydrous calcium chloride. Because of its great solubility it is employed to prepare solutions used at low temperatures in refrigeration. A mixture of the salt with its solution and ice does not attain equilibrium until a temperature of −55° C. is reached. Other uses are for laying dust on roads and in subways. This is due to the ability of the salt to take up water from the atmosphere and thus remain moist. Numerous unsuccessful attempts have been made to use its solutions as a cooling medium in automobile radiators, but this practice is objectionable because of corrosion.

Calcium hypochlorite, $Ca(OCl)_2$, is slightly soluble in water, and gives an odor of free chlorine, because of hydrolysis. The theoretical compound, $Ca(OCl)_2$, is less important than a double salt $CaCl(OCl)$ sold as **bleaching powder, chloride of lime** or **chlorinated lime.** This is the product resulting from passing chlorine gas over slaked lime in thin layers. The reaction is never complete and the aqueous solution of the product is always basic in reaction. It gradually decomposes in the air and is therefore handled in sealed drums or in small cans. In essence these products merely furnish a means of handling chlorine, and are of value for their bleaching and disinfectant action. Calcium hypochlorite is evaluated at about 65 per cent available chlorine and bleaching powder at 35-37 per cent. Applications are in milk plants, textile bleaching, water sterilization, etc. Use of these calcium compounds has been declining for many years because of the development of methods for the direct handling and use of chlorine on the one hand, and the sale of chlorine bleach liquor, which is sodium hypochlorite, on the other.

Calcium bromide, $CaBr_2$, is a deliquescent salt, very soluble in water or alcohol. It forms hydrates, $CaBr_2,2H_2O$ and $CaBr_2,6H_2O$. The major properties are similar to those of the chloride. It is produced by the reaction of calcium carbonate, oxide or hydroxide with hydrobromic acid. The U.S.P. grade is the dihydrate, containing 84-94 per cent of the salt on a dry basis. The usual commercial grade is the hexahydrate. Because of its relatively high price its sale is limited. Typical uses are in medicine and photography.

Calcium iodide, CaI_2, is a deliquescent and exceedingly soluble salt prepared by the solution of calcium oxide, hydroxide or carbonate in hydriodic acid. It forms a hydrate, $CaI_2,6H_2O$ and is used in medicine.

Calcium fluoride, fluorite, or **fluorspar,** CaF_2, occurs naturally. It is insoluble in water, only slightly soluble in concentrated acids and is the principal commercial source of fluorides. It contains various impurities, so that the mineral may be found in almost every color. Calcium carbonate, silica, lead, zinc and iron are among the contaminants which may be present. Both domestic and foreign grades reach the market under such classifications as acid-grade, 98 per cent; enamelers, 96-98 per cent; standard washed gravel, 85 per cent; and powdered, 97 per cent. Aside from being a source of fluorides it is used in metallurgy, as in open hearth steel furnaces, and in the manufacture of opalescent glass and enamelware.

Calcium phosphate, or **calcium orthophosphate,** may refer to any of three salts. **Monocalcium phosphate, monobasic calcium phosphate,** or **primary calcium phosphate,** $CaH_4(PO_4)_2,H_2O$, is moderately soluble in cold water. It is made by the appropriate degree of neutralization of phosphoric acid with lime or calcium hydroxide. Its aqueous solution is slightly acid. A highly purified grade is used in baking powder. It is the major active ingredient of superphosphate, a fertilizer material.

Dicalcium phosphate, dibasic calcium phosphate or **secondary calcium phosphate,** $CaHPO_4,2H_2O$, is almost insoluble in water. It is precipitated by the reaction of calcium chloride and disodium orthophosphate. A precipitated grade containing the equivalent of 38-42 per cent of phosphorus pentoxide is sold for use in special fertilizers and medicine.

Tricalcium phosphate, tribasic calcium phosphate, or **tertiary calcium phosphate,** $Ca_3(PO_4)_2$, is an insoluble compound which may be produced by the reaction of calcium chloride, trisodium phosphate and ammonia. It is used in ceramics, in making porcelain, enamel and milk-glass. A precipitated form is used as an abrasive in products such as tooth paste. **Bone ash** consists principally of tricalcium phosphate and is used for the same purposes. **Phosphate rock**, which occurs naturally, consists largely of tricalcium phosphate. It is quarried in different places, such as in Florida, where it is sold as high grade, hard, 77 per cent; and land-pebble, 68, 70, 72, 74, 75, and 76 per cent minimum. The Tennessee rock is sold in 72 and 75 per cent grades. Phosphate rock is the primary source of phosphorous compounds.

Superphosphate is a mixture of hydrated monocalcium acid phosphate and calcium sulfate, produced by the action of sulfuric acid on phosphate rock. It is quoted on the basis of phosphorus pentoxide, P_2O_5, content. Grades sold are guaranteed 16 per cent run-of-pile, basis 16 per cent; and triple, 44-45 per cent. It is used in fertilizer as a source of available phosphate.

Bone is recovered from animals after the other parts are utilized. It is mainly valuable because of its phosphorus content, since the principal constituent is tricalcium phosphate. Organic nitrogen compounds are also present. **Steamed bone meal** is produced by steaming the bones under pressure and then drying and grinding. Typical grades sold are raw, 4½ per cent ammonia, 50 per cent phosphate, steamed 1½ per cent ammonia, 60 per cent phosphate; or 1-1¼ per cent ammonia, 60-70 per cent phosphate; steamed bone meal, domestic, 3 per cent ammonia, 50 per cent phosphate; and imported grades. It is used in fertilizer mixtures, furnishing both nitrogen and phosphorus.

Hoof meal, which consists largely of tricalcium phosphate, is prepared by cooking the hoofs of animals until they become friable,—drying and grinding. A typical grade contains the equivalent of 17-18 per cent of ammonia. It is used in fertilizer mixtures.

Calcium hypophosphite, $Ca(H_2PO_2)_2$, is very soluble in water. It is produced by neutralization of hypophosphorous acid with lime or calcium hydroxide, and is used in medicine.

Calcium nitrate, lime nitrate, or **lime saltpeter,** $Ca(NO_3)_2$, is an extremely soluble, deliquescent salt. The usual form is a hydrate, $Ca(NO_3)_2{,}4H_2O$. It is produced in the arc process for fixing atmospheric nitrogen, when oxides of nitrogen are converted to nitrates with lime as the alkali. The same reaction applies when ammonia is catalytically oxidized to nitric acid. It may be used as fertilizer or treated as an intermediate stage in the preparation of other nitrates.

Calcium carbide, CaC_2, is unstable in the presence of water, reacting to liberate acetylene and forming hydrated lime. It is manufactured by heating lime and carbon together in an electric furnace. The once important market for production of acetylene as an illuminant, has dwindled almost to the vanishing point. The corresponding market for production of acetylene for use as an intermediate in synthetic organic chemistry is growing, rather than declining. If nitrogen is present in the electric furnace as used for the manufacture of calcium carbide, further reaction occurs, forming **calcium cyanamide,** $CaCN_2$, called in the trade simply **cyanamide.** This is a black lump or powdered material. It reacts slowly with water to liberate ammonia and formed the basis of one process for the fixation of nitrogen. While important at the time of the World War, this process is fast becoming obsolete because of the economies of direct synthesis. The commercial grade contains 21-22 per cent of nitrogen and is sold at quotations per ammonia unit. Cyanamide is used as an intermediate stage in the manufacture of other chemicals, in metallurgy and as a fertilizer.

Calcium silicate, or **tricalcium silicate,** is a complex material which is not an article of commerce as such. **Cement** or **Portland cement** is a grey, finely powdered calcium-silicate material which sets after mixing with water, and which is believed to form hydrated tricalcium silicate along with some dicalcium silicate. It is insoluble in water but nearly completely soluble in hydrochloric acid, either before or after setting. **White cement** differs only in the more careful selection of raw materials for freedom from iron. Cement is made by fusion of marl, or a mixture of chalk or limestone, and clay or shale. After heating, the resulting clinker is ground. Sometimes the original mixture is ground wet and passed to the kiln in the form of a slurry. This meets with hot gases which dry it out, and then it goes to a hotter zone where lime combines with silica and alumina and the mass partially fuses. The clinker is then ground to the desired fineness.

Cement is a standard item from various manufacturers, and conforms to specifications of the American Society for Testing Materials. An average composition is SiO_2, 21.85 per cent; Fe_2O_3, 2.62 per cent; Al_2O_3, 7.03 per cent; CaO, 62.5 per cent; MgO, 2.06 per cent; SO_3, 1.38 per cent; and loss on ignition, 1.80 per cent. Maximum allowances are loss on ignition, 4.00 per cent; residue insoluble in hydrochloric acid, 0.85 per cent; SO_3, 2 per cent; MgO, 5 per cent. The ratio of lime to silica and alumina, calculated in chemical equivalents, is to be between 2 and 2.9. There are also physical specifications. Cement is the binding agent used in making concrete for all kinds of structural purposes—roads, dams, piers, bridges, buildings, ornamental work on buildings, etc. **Mortar** is the general term used for a mixture of 3 parts of sand and one of Portland cement by volume, when mixed with water. **Concrete** is this same mixture with substantial volumes of crushed stone added, usually 3 to 5 volumes. Calcium silicate is therefore one of the important water-insoluble calcium salts, although not quoted as such. **Aluminous cement or ciment**

fondu is similar to Portland cement but has a high aluminum content and is quicker setting.

Calcium arsenate or **tricalcium arsenate,** $Ca_3(AsO_4)_2,3H_2O$, is very slightly soluble in water. It is produced by the reaction of sodium arsenate and calcium chloride. It is used as an insecticide in large volume, particularly against the boll weevil. It is also a fungicide. Application is by dusting, the solubility being so low that it remains effective for a relatively long time rather than being quickly dissolved away by rain water.

Calcium ferrocyanide, $Ca_2Fe(CN)_6,12H_2O$, is a yellow crystalline compound, only slightly soluble in cold water but very soluble in hot. It occurs as an intermediate in the manufacture of the sodium salt and is also produced from Prussian blue and lime by heating with steam and crystallizing. Uses are varied, such as in precipitation of iron present as impurity in organic acid solutions, preparation of other ferrocyanides, etc.

Calcium acetate, $Ca(O_2CCH_3)_2,H_2O$, is very soluble in water and slightly soluble in alcohol. It has numerous other names such as **lime acetate, acetate of lime, vinegar salts,** etc. The pure form is made by reaction of acetic acid with slaked lime. Formerly it was prepared in large amounts from the crude pyroligneous acid resulting from wood distillation. As such it was known as **brown acetate, gray acetate,** or **lime pyrolignite.** Many factors have combined to reduce the importance of wood distillation, principally synthetic methods for the production of methyl alcohol, acetone and acetic acid. The crude calcium acetate is washed and otherwise purified, after which it is decomposed with sulfuric acid and the purified acetic acid distilled. Similarly calcium acetate is dry-distilled to produce acetone. Further decline in these uses can be expected. The calcium acetate is mainly a stage in purification of acetic acid or in the production of acetone, not an end-product. Good-quality salt is used to a limited extent as a mordant in the dyeing and printing of textiles.

Calcium lactate, $Ca[O_2CCH(OH)CH_3]_2$, is very soluble in cold water, extremely soluble in hot and slightly soluble in alcohol. It is formed by the reaction of calcium carbonate with lactic acid. The U.S.P. grade is a pentahydrate containing

25-30 per cent of water and not more than 2 per cent of other impurities. It is used in medicinals and food products as a source of assimilable calcium.

Calcium glycerophosphate, $Ca(C_3H_7O_6P)_2$, is a hygroscopic water-soluble material produced by the reaction of glycerine with phosphoric acid, and subsequent neutralization with lime slurry. It is used in medicine.

Calcium soaps are water-insoluble but dissolve or disperse to form jelly-like structures in petroleum oils. They are therefore used to solidify oils to produce greases, often being manufactured in the oil by reaction of the suitable fatty acid and lime. They are not sold under the general term of calcium soaps but specific soaps are sold for numerous purposes.

Calcium stearate, $Ca[O_2C(CH_2)_{16}CH_3]_2$, which is insoluble in water but soluble in alcohol or ether, is obtained by the reaction of sodium stearate and a soluble calcium salt such as the chloride. The precipitated grade is sold. Its main use is as a waterproofing agent.

Calcium palmitate, $Ca[O_2C(CH_2)_{14}CH_2]_2$, is similar to the stearate in properties, methods of manufacture and use.

Calcium resinate is an insoluble soap, a crude form of **calcium abietate,** $Ca(O_2CC_{19}H_{29})$, obtained by boiling rosin with lime water and subsequently filtering. It is also produced by the reaction of sodium abietate, which is water-soluble, with suitable soluble calcium salts such as the chloride or bicarbonate. The precipitated grade is quoted for use as a paint drier and as a waterproofing agent.

Calcium gluconate, $Ca[O_2C(CHOH)_4CH_2OH]_2.H_2O$, is moderately soluble in cold water and very soluble in hot. It is produced from gluconic acid and lime slurry and is sold as a U.S.P. grade in granular or powdered forms, for use in medicinals. The U.S.P. grade contains the equivalent of 12.4-12.8 per cent of calcium oxide.

Calcium sulfocarbolate or **calcium phenolsulfonate,** $Ca(SO_3C_6H_4OH)_2,5H_2O$, is a water- and alcohol-soluble compound obtained by the reaction of phenolsulfonic acid and lime slurry. It is used as an antiseptic and disinfectant.

CHAPTER IX

BARIUM, STRONTIUM AND MAGNESIUM COMPOUNDS

Barium, Ba, is a metal similar in general properties to calcium. It is of no importance as a free metal. The compounds are closely related to those of calcium but in general are more expensive. Nearly all barium compounds are white when pure. Those which are soluble in water are poisonous.

Barium carbonate, $BaCO_3$, is insoluble in water but soluble in those acids which form water-soluble barium salts. It occurs naturally as **witherite,** and is also formed by precipitation with barium chloride or other soluble barium salt, from a hot solution of ammonium carbonate or other soluble carbonate. The natural product is ground and sold as 90 per cent and 99 per cent through a 200-mesh sieve. Impurities in the natural product are calcium, silica, iron, alumina, etc. Precipitated barium carbonate and a special sulfur-free grade are quoted. Barium carbonate is used as the basis for manufacture of many other barium salts and as the usual commercial source of barium as a compound. It is also used as a neutralizing agent for sulfuric acid in the synthetic dyestuff industry, as an ingredient of crown glass, as a rat poison, in rubber compounding, and for many other purposes.

Barium oxide or **barium monoxide,** BaO, is a white to yellow or gray powder. It reacts with water to form barium hydroxide, which is slightly soluble. It is soluble in acids which form soluble barium salts. Ignition of barium nitrate or of the carbonate produces the oxide of a degree of purity dependent on that of the raw material. The usual grade is from ignition of a good grade of carbonate. Barium oxide reacts readily with the moisture and carbon dioxide of the air and is therefore apt to be contaminated with the hydrate and carbonate. Iron may also be present as an impurity. It is used in the preparation of other barium salts, for preparation of

barium hydroxide or **barium hydrate,** used as an alkali, and in ceramics.

Barium dioxide or **barium peroxide** is a grayish to white powder. Both the anhydrous form, BaO_2 and a hydrate, $BaO_2.8H_2O$, are known. It is insoluble in cold water, decomposed by hot water and soluble in acids. Barium dioxide is considered to be the barium salt of hydrogen peroxide. It is prepared from barium oxide by heating it in a current of oxygen. When treated with sulfuric acid, barium sulfate and hydrogen peroxide are obtained, a reaction applied in making the latter compound. It is also used in pyrotechnics and to some extent in the preparation of other barium salts.

Barium sulfate, $BaSO_4$, occurs naturally as **barytes, barite,** or **heavy spar.** The natural mineral may contain up to 5 or even 10 per cent of impurities. When ground it is sold as barytes. Various grades sold include domestic floated, southern off-color, domestic 95 per cent, imported German ground, imported Italian ground, and unground. It is used as an extender for paint pigments and as a filler for paper, rubber, etc.

Blanc fixe is precipitated barium sulfate. It may be prepared by precipitating a solution of a barium salt with sodium sulfate, or as a by-product in the manufacture of hydrogen peroxide from barium dioxide. The precipitated salt is finer and whiter than the natural product. Grades are dry by-product, high-grade precipitated, 66 2/3 per cent pulp; and X-ray. It is used for many of the same purposes as barytes. By precipitation of organic lakes on it, colored pigments are produced. Because of its insolubility it is taken internally to produce a dense shadow of the digestive organs in X-ray work.

Barium chloride, $BaCl_2,2H_2O$, is very soluble in water but unlike calcium chloride, is not deliquescent. It is obtained by dissolving natural barium carbonate in hydrochloric acid. Another method is by igniting natural barium sulfate with coal, calcium chloride and limestone. The resulting barium chloride is then extracted with water. C.P. and technical 99 per cent crystals are quoted. It is used chemically in numerous industries where a soluble barium compound is needed.

Barium iodide, $BaI_2,2H_2O$, is a salt extremely soluble in water and very soluble in alcohol. It is obtained by the neutralization of barium hydroxide by hydriodic acid or by the double decomposition of barium carbonate and ferrous iodide. It is used for the preparation of other iodides and in medicine.

Barium fluoride, BaF_2, is a slightly soluble salt obtained by the reaction of soluble barium compounds with hydrofluoric acid. It can be produced by the reaction of barium sulfide and hydrofluoric acid. Typical uses are as a poison and antiseptic, in the manufacture of enamels and in embalming fluids.

Barium fluosilicate, $BaSiF_6$, is a slightly soluble salt manufactured by reaction of the hydroxide with fluosilicic acid. It is used as an insecticide.

Barium chlorate, $Ba(ClO_3)_2,H_2O$, is very soluble in cold water and exceedingly soluble in hot. It results from the double decomposition of barium chloride and sodium chlorate or by passing chlorine into a boiling aqueous suspension of barium carbonate. It is used for the manufacture of other chlorates and in explosives and pyrotechnics. In the latter case barium compounds are of value for producing green colors.

Barium nitrate, $Ba(NO_3)_2$, is moderately soluble in cold water but very soluble in hot. It is prepared by dissolving a readily available barium compound, such as the carbonate, in dilute nitric acid, or by mixing hot solutions of crude sodium nitrate and barium chloride, from which sodium chloride is precipitated. It is used in explosives and pyrotechnics.

Strontium is a metal very much like calcium and having no important commercial applications as the element. Its compounds are similar to those of calcium and unimportant commercially in tonnage. They are relatively expensive. The salts are white when pure.

Strontium carbonate, $SrCO_3$, is highly insoluble in water but soluble in acids such as hydrochloric, nitric and sulfuric. It occurs naturally as **strontianite,** or may be formed by the fusion of naturally occurring strontium sulfate, **celestite,** with sodium carbonate. The grade sold is of good quality. Strontium carbonate is used in the manufacture of other strontium compounds and in special glasses.

Strontium nitrate, $Sr(NO_3)_2$, is very soluble in cold water and extremely soluble in hot. It also forms a hydrate $Sr(NO_3)_2,4H_2O$. The nitrate is made from strontium sulfate by reducing it to the sulfide by means of carbon and driving off hydrogen sulfide with dilute nitric acid. It is also made by dissolving the carbonate in dilute nitric acid. Both imported and domestic grades are quoted. Uses are in pyrotechnics, marine signals and railroad flares, as it imparts a carmine-red color to flame.

Strontium bromide, $SrBr_2$, is very soluble in cold water and extremely soluble in hot. It forms a hydrate, $SrBr_2,6H_2O$. It also dissolves in alcohol. The product is made by treating strontium carbonate with hydrobromic acid or with bromine in the presence of a reducing agent. It is used in medicine.

Strontium iodide, SrI_2, is even more soluble than the bromide and forms a similar hydrate. It results from treating strontium carbonate with hydriodic acid, and is used in medicine.

Magnesium is a silvery white metal which, while relatively expensive, is important as an element in light-weight alloys. The metal when finely subdivided burns readily to the oxide. It is the active ingredient which burns with barium chlorate in flashlight powder, which is now rapidly becoming obsolete, being replaced by flashlight bulbs. In massive form it does not burn in that way. The compounds are closely related to those of calcium. Because of the wide distribution of its compounds in the earth's crust, the natural ores and their derivatives are inexpensive. The compounds are often tonnage items and are usually white. They are often termed magnesia compounds although that term is correctly the name of the oxide.

Magnesium carbonate, $MgCO_3$, occurs naturally as **magnesite.** It is widely distributed and also occurs with calcium carbonate in dolomitic limestone. It is insoluble in water. The crude material may be ground and purified by leaching out soluble impurities. It is also made by precipitation of a soluble magnesium salt with a soluble carbonate, as for example from magnesium chloride and soda ash. Both the ground and precipitated grades are quoted. Magnesium carbonate is the usual source of the oxide from which various magnesium salts are produced, but the chloride is also of importance for this purpose. The carbonate is used as a fine polishing agent, in ceramics, in rubber, and in heat insulation.

Basic magnesium carbonate or **magnesia alba,** $Mg(OH)_2$, $3MgCO_3,3H_2O$, is produced by treatment of wet magnesium oxide or hydrate with carbon dioxide, and probably by other means. U.S.P. and technical grades are quoted. The U.S.P. is a hydrated basic rather than normal carbonate, equivalent to 39.2-41.5 per cent of magnesium oxide. It is used in medicine.

Magnesium oxide or **magnesia,** MgO, is insoluble in water. It is soluble in acids and absorbs moisture and carbon dioxide slowly from the air. The oxide is prepared by heating magnesium carbonate or basic magnesium carbonate. The former gives a very light powder, the latter a heavier powder. Magnesia is highly infusible or refractory, and nonvolatile. Its heat conductance is very low. Quoted grades include technical heavy, U.S.P. heavy, U.S.P. special, U.S.P. light, and U.S.P. super light. The U.S.P. standard for either light or heavy grades requires at least 96 per cent magnesium oxide after ignition and not over 10 per cent loss in weight on ignition. **Calcined magnesite** or **calcined magnesia** is a special grade, calcined at a temperature to make it very reactive with magnesium chloride in producing indefinite double compounds known as **magnesia cements** or **Sorrel cements.** These cements are cast as small objects, tiles, etc. and are used for troweled-on types of light-weight flooring such as on ships' decks. Calcined magnesias are of both domestic and foreign origin. Heavy calcined magnesia is used in the vulcanization of rubber. **Dead-burned magnesia** is also important, having been calcined at a higher temperature. The distinctive properties of this oxide make it useful as a heat insulator and as a refractory material in lining furnaces, making crucibles, etc. The oxide is used as an antiacid in medicine, as a basic material for producing other magnesium compounds, as a fine abrasive and as an inexpensive filler. When the oxide has completely reacted with water in the absence of carbon dioxide the product is **magnesium hydroxide or magnesium hydrate,** $Mg(OH)_2$. A suspension of this in water is **milk of magnesia,** used as a mild alkali and in medicine. While the suspension of the hydroxide is alkaline it is not of importance as an alkali.

Magnesium peroxide, MgO_2, is practically insoluble in water but soluble in acids. It is formed by the reaction of a concentrated solution of magnesium sulfate with barium peroxide. A grade containing 15 per cent of active oxygen is quoted. It is used as an antiseptic and as an oxidizing and bleaching agent.

Magnesium sulfate occurs naturally as **kieserite** but is largely manufactured by the reaction of sulfuric acid and magnesium oxide or carbonate. The usual form is the hydrate, $MgSO_4,7H_2O$, which is known as **Epsom salt.** It is quoted as technical, U.S.P. crystals, domestic and imported, and dried, the latter being anhydrous, $MgSO_4$. The U.S.P. grade contains 45 to 52 per cent of water, and not less than 99.5 per cent of the anhydrous salt on ignition. Calcined kieserite containing 96-98 per cent of magnesium sulfate is also sometimes quoted. The material is used in tonnage as a fireproofing agent, for weighting of textiles, as sizing, and as a medicinal.

Magnesium chloride has much in common with calcium chloride. It exists as the anhydrous salt, $MgCl_2$, and forms a hexahydrate, $MgCl_2,6H_2O$. It occurs in sea water, and in certain mineral deposits, both alone and in combination with potassium chloride. The salt hydrolyzes with the formation of free hydrochloric acid, which gives it its corrosive action in solution, particularly when heated. A flake salt is sold. It is very deliquescent, which makes it useful as a dust-laying compound. It is also used as a fireproofing agent, for the sizing of textiles and papers, in ceramics, for the preparation of other magnesium salts, and as a fire extinguisher. When it reacts with properly calcined magnesite it forms magnesia cement or Sorrel cement.

Asbestos is a form of impure **magnesium silicate** occurring in long, delicate fibers or in fibrous masses, colored white, gray or greenish gray and varying considerably in composition. **Serpentine asbestos** is the type most used and consists of long, strong, silky fibers, largely composed of a hydrous magnesium silicate. **Amphibole asbestos** is usually a mixture of iron, calcium and magnesium silicates with little or no bound water. This type is more stable chemically and more resistant to acids and heat, but the fibers are of low tensile strength and cannot be spun. Practically all supplies are imported from a few Canadian sources. Grades of asbestos sold are 5M, 5R, 6D, 7D, 7F, 7H, 7K and 7M, the last grade 7M having only about a third of the value of the first, 5M. Serpentine asbestos is used in making fireproof textiles, clothing, curtains, filter cloth, ropes, heat-proof and electrical insulating materials, brake lining, pipe covering, roofing paper, cement, plaster, in rubber compounding, etc. Amphibole asbestos is used in making chemical filters and as a paint extender.

Talc is another form of magnesium silicate approximating acid magnesium metasilicate, $H_2Mg_3(SiO_3)_4$. It occurs naturally in foliated, granular or fibrous masses. The mineral is very soft, with a soapy feel and is sometimes called **mineral graphite** or **soapstone.** It is usually white, greenish or grayish in color and is insoluble in water or acids. Talc is very soft, having a value of 1.5-2.5 on Moh's scale of hardness. Gradings shade into the asbestos field. Other related minerals are sometimes sold as talc, and at least one sold as talc is by structure pyrophyllite, an alkali-metal aluminum silicate. Among the domestic grades sold are the following: Californian numbers 1 and 2, of which number 1 is the better grade; New York, fibrous, 93-94 per cent through 325 mesh, 96-98 per cent through 325 mesh, 99.85-99.95 per cent through 325 mesh, and coarse, off-color; Ohio, alumina-magnesia type, ground; and Vermont. Imported grades are Canadian, French ordinary and high-grade, and Italian 1 and 2. The imported qualities command a large premium and are preferred by the trade for fine products. Talc is used as a filler in paper, plastics, insulating compositions, linoleum, etc. It is used as an industrial dusting powder for such products as rubber and foundry molds. Good grades are used in cosmetics and toilet preparations and as personal dusting powders. Thus the uses range from coarse fillers to the finest face powder, in all cases being present as an inert rather than as a chemically reactive material. It is an important element of ceramic bodies. **Asbestine** is a trade name for a grade used in paint. **Talcum powder** is often largely talc.

Metronite is a mineral consisting largely of magnesium silicate and calcium and magnesium carbonates. It is refined for sale as 120, 180, 250 and 325 mesh grades. Use is mainly as a paint extender, the prices being such as to compete with the grades of talc and whiting which are similarly applied.

Magnesium silicofluoride or **magnesium fluosilicate,** $MgSiF_6$, is the water-soluble product formed by the reaction of magnesium carbonate with hydrofluosilicic acid. It is used in ceramics and as a hardening agent in concrete.

Magnesium hypophosphite, $Mg(H_2PO_2)_2,6H_2O$, is the very soluble product obtained by the reaction of magnesium oxide with hypophosphorous acid. It is also obtained by the reaction of magnesium oxalate and calcium hypophosphite and is used in medicine.

Magnesium arsenate, $Mg_3(AsO_4)_2,XH_2O$, is a water insoluble material, usually off-color due to impurities. It is highly hydrated, but to a variable degree. The material results from the reaction of magnesium carbonate and arsenic acid, or by combining the manufacture of arsenic acid from arsenious oxide with conversion to the magnesium salt. It is used as an insecticide.

Magnesium soaps are insoluble in water and similar in general properties to calcium soaps. **Magnesium stearate,** $Mg[O_2C(CH_2)_{16}CH_3]_2$, is formed by the reaction of soluble magnesium salts with sodium stearate and is used as a drier in protective coatings. The properties, manufacture and uses of **magnesium palmitate,** $Mg[O_2C(CH_2)_{14}CH_3]_2$, are similar.

CHAPTER X

COMPOUNDS OF NICKEL, COBALT, MANGANESE AND ZINC

Nickel, Ni, is a silvery metal which is important industrially, its use being limited only because of its cost. Deposits of ore are largely in Canada. After smelting the oxide from the ore, which is usually a silicate or a sulfide, the metal is produced by reduction and refined electrolytically. **Pentalandite** is a typical ore, a nickel, copper, iron sulfide. Nickel is an alloying element rather than one to be used in the pure form, nickel steels being very hard and tough as compared with ordinary steels. One of the ores smelted directly yields a commercial nickel-copper alloy containing a small amount of iron and is sold as **Monel metal.** In general the hydrated salts of nickel have a green color and the anhydrous a yellow color. The metal is somewhat soluble in dilute acids and the soluble salts are poisonous. Decline of the nickel-plating industry in recent years has lessened the importance of the salts, while use of the metal in alloys has increased. The finely divided metal resulting from reduction of the oxide or a suitable salt, is used as a catalyst for the hydrogenation of saponifiable oils.

Nickel oxide, NiO, is green. When it is heated and allowed to absorb more oxygen the new oxide is black, Ni_2O_3. Both oxides are insoluble in water but soluble in acids or ammonium hydroxide. Nickel oxide occurs naturally, or may be obtained by carefully heating the nitrate, carbonate, hydroxide or sulfate. It is used for the preparation of nickel salts, in the decorating of porcelain and as a catalyst.

Nickel carbonate is a green insoluble salt. It is basic, having approximately the formula $NiCO_3,2Ni(OH)_2,4H_2O$, rather than the normal carbonate formula, $NiCO_3$. It is soluble in acids and in solutions of ammonium salts. The compound is precipitated from solutions of soluble nickel salts by addition of a soluble carbonate such as sodium carbonate. It is used as an intermediate in the preparation of some nickel salts and as a green coloring material in glazes.

Nickel chloride, $NiCl_2,6H_2O$, is a green, deliquescent salt, extremely soluble in water, very soluble in alcohol and soluble in solutions of ammonium hydroxide. It is produced by treating nickel oxide or nickel carbonate with hydrochloric acid. The anhydrous salt is yellow and can be obtained by heating the hydrated salt to 140° C. Nickel chloride is used as an antiseptic, for nickel-plating, as an absorbent for ammonia gas in gas masks, and in minor products.

Nickel sulfate, $NiSO_4$, is yellow and very soluble in water. As the hexahydrate, $NiSO_4,6H_2O$, it is also very soluble in alcohol and blue in color. The properties of the heptahydrate are similar but the color is green. **Single nickel salt** is the heptahydrate, $NiSO_4.7H_2O$, obtained by dissolving nickel, nickel oxide, carbonate or hydroxide in dilute sulfuric acid containing a small amount of nitric acid. The heptahydrate changes to a lower hydrate when heated to 100° C., and to the anhydrous salt at 300° C. Nickel sulfate is used in nickel plating, as a mordant, in coloring metals, in ceramics and for producing driers for use in protective coatings.

Double nickel salt or **nickel ammonium sulfate,** $NiSO_4,(NH_4)_2SO_4,6H_2O$, is moderately soluble in cold water, very soluble in hot. It is produced by treating a solution of nickel sulfate containing sulfuric acid, with ammonium sulfate. Uses are largely in electroplating.

Cobalt, Co, is a metal closely related to nickel. As such it is unimportant but the salts have substantial use in industry. The cobaltous salts are generally pink if hydrated, and blue if anhydrous. A series of higher valence cobaltic salts are unimportant. The ores are arsenides or sulfides.

Cobalt carbonate or **cobaltous carbonate** is a red compound prepared by the reaction of sodium carbonate with cobaltous acetate. As cobaltous carbonate is insoluble in water, it precipitates from solution as a basic salt, $2CoCO_3.3Co(OH)_3$. It is sold as a technical grade and is used in manufacturing cobalt salts and pigments.

Cobalt oxide or **cobaltic oxide,** Co_2O_3, is a gray to black powder insoluble in water but soluble in strong acids and soluble in ammonium hydroxide solution. It is obtained by dehydrating and oxidizing cobaltous hydroxide by direct heating, and is used as a pigment and for coloring glass, enamels and glazes. The deep blue product, when dissolved, is popularly described as cobalt blue, and the term cobalt is even used as a synonym for blue. The term **cobalt blue** is applied in the trade to an impure cobalt oxide which has been fused with aluminum compounds. This is also of a deep blue color and used mainly for coloring enamels and glazes. It dissolves more readily than cobalt oxide. Cobalt blue is also an expensive pigment.

Smalt, Saxony Blue or **azure blue,** is a blue amorphous insoluble powder. It is formed by fusing together potash, silica and cobalt oxide and grinding the glass thus formed to a powder. Smalt has been used as a pigment, for coloring paint, paper, textiles, starch, etc., but is largely replaced by ultramarine. In a darker form it is known as **black smalt.**

Cobaltous hydroxide or **cobalt hydrate,** $Co(OH)_2$, is a red, amorphous powder insoluble in water but soluble in acids or ammonium salt solutions. It is prepared by adding sodium hydroxide to a solution of a cobaltous salt. The hydroxide is produced as one step in the refining of cobalt ores, usually admixed with nickel hydroxide. It is used in preparing salts of cobalt and for the preparation of driers for use in protective coatings.

Cobalt sulfate, or **cobaltous sulfate,** exists as an anhydrous form, $CoSO_4$, but is normally the heptahydrate, $CoSO_4.7H_2O$. Both are red, very soluble in water and soluble in alcohol. The product results from the action of sulfuric acid on cobalt oxide. It is used in making cobalt glass, in cobalt plating and in the preparation of other compounds.

Cobalt chloride or **cobaltous chloride,** forms a blue anhydrous salt, $CoCl_2$, and a pink hydrate, $CoCl_2,6H_2O$. Both are very soluble in water, alcohol, ether or acetone. They are produced by solution of the oxide or carbonate in hydrochloric acid, and evaporation. The impure chloride is produced in refining cobalt ore, contaminated with nickel chloride. The commercial hydrated salt is used in electroplating and as a coloring substance in liquids. In anhydrous liquids the color is blue, and in water or hydrous liquids, pink. This property is also the basis for use of this and other cobalt salts in "sympathetic" inks, those invisible until developed, usually by heating.

Cobalt acetate or **cobaltous acetate,** $Co(O_2CCH_3)_2{,}4H_2O$, is a soluble, red, deliquescent salt obtained by neutralizing cobaltous hydroxide with acetic acid and evaporating. It is used in "sympathetic" ink, in coloring oilcloth, and in preparing other cobalt compounds.

Cobalt oleate or **cobaltous oleate,** $Co[O_2C(CH_2)_7CH{:}CH(CH_2)_7CH_3]_2$, is a brown, amorphous powder, insoluble in water but soluble in oils, alcohol, or ether. It is obtained by boiling a solution of sodium oleate and cobaltous chloride. The main use is as a varnish drier.

Cobalt linoleate or **cobaltous linoleate,** $Co[O_2C(CH_2)_7CH{:}CHCH_2CH{:}CH(CH_2)_4CH_3]_2$, is similar in properties, preparation and uses to cobalt oleate. Commercial grades are paste 6 per cent, and solid 8½ per cent, classified by cobalt oxide content.

Cobalt resinate or **cobaltous resinate,** is a crude form of **cobalt abietate,** $Co(O_2CC_{19}H_{29})_2$, prepared by fusing rosin and a cobaltous compound. Grades are fused A, and 1, 2 and 3 per cent. A precipitated grade is prepared by boiling together sodium resinate and a cobalt salt in aqueous solution. This is much higher in cobalt oxide, more expensive and more effective. These resinates are used as varnish driers.

Manganese, Mn, is a gray, hard metal, which is soluble in acids. The principal ore is manganese dioxide but other oxides, sulfides and carbonates are found. Iron minerals are usually associated with them. The reduction of the ores is complex, usually carried out with the aid of aluminum. The metal is used for alloying in steel to give hardness and toughness.

Compounds of manganese are widely used in the arts. The element combines both in the positive and negative radicals. As a positive element the usual manganous salts are pink to red. A series of manganic salts exists but these are unimportant. Insofar as manganese is important as an acid-forming element it has been discussed under the appropriate salt. The major commercial form is as potassium permanganate. Other complex forms with manganese in the negative radical exist.

Manganese dioxide or **manganese peroxide,** MnO_2, is a gray to dark green or black substance, insoluble in water but soluble in acids. It occurs naturally as **pyrolusite,** usually somewhat impure. The pure oxide is prepared by igniting manganous nitrate, or by heating manganous carbonate in the presence of air and washing the residue with cold dilute hydrochloric acid. Manganese dioxide is a strong oxidizing agent. The usual commercial grade is Caucasian 85-90 per cent dioxide. A 50-52 per cent ore is also quoted. It is used in various processes as an oxidizing agent, in glass making for decolorizing ferrous iron, to promote combustion in matches, in dye manufacture, in the production of pigments, in dry batteries, in steel manufacture and for production of other manganese compounds.

Manganese hydrate or **hydrated manganic oxide** is $MnO(OH)$, a brown powder which forms when the light pink manganese hydroxide, $Mn(OH)_2$ is exposed to the air. It is insoluble in water but soluble in acids and is precipitated when alkali is added to a solution of a manganous salt. Uses are in ceramics and as an assist in printing or dyeing textiles.

Manganese carbonate, $MnCO_3$, is an insoluble rose-colored powder. It is precipitated by the reaction of a solution of manganese sulfate or chloride with a solution of sodium carbonate, and is used for manufacture of other manganese salts.

Manganese sulfate or **manganous sulfate** forms various pink hydrates. The anhydrous salt, $MnSO_4$, and the tetrahydrate, $MnSO_4,4H_2O$, are the usual forms. They are very soluble in water and are of commercial importance. The sulfate is formed by heating manganese dioxide with sulfuric acid. Commercial grades are anhydrous, 90-95 per cent, 80-85 per cent, and 65 per cent. They are used in manufacture of other salts, in glazes and for numerous minor purposes.

Manganese chloride or **manganous chloride,** $MnCl_2,4H_2O$, is a red, deliquescent salt, very soluble in water and slightly soluble in alcohol. Boiling manganese dioxide with hydrochloric acid produces the chloride and liberates free chlorine. A pure grade is made by the reaction of hydrochloric acid and the carbonate, with concentration of the solution formed. It is used for preparation of other salts, for preparation of catalysts, and in dyeing and printing of textiles.

Manganese iodide or **manganous iodide,** $MnI_2,4H_2O$, is a very soluble, deliquescent, red salt formed by the reaction of manganous hydroxide with hydriodic acid. It is used in medicine.

Manganese borate, MnB_4O_7, is a water-soluble pink powder formed by the reaction of manganous hydroxide with boric acid. It is used as a drier in protective coatings.

Manganese arsenate is a pink, nearly insoluble salt of complex structure formed from water-soluble arsenates and soluble manganese salts for use as an insecticide.

Manganese acetate, $Mn(O_2CCH_3)_2,4H_2O$, is a red salt, soluble in water or alcohol, formed by the reaction of acetic acid with manganous hydroxide, $Mn(OH)_2$. It is used as a drier in protective coatings, in the finishing of leather, as a mordant in dyeing textiles, and as a catalyst in oxidation processes.

Manganese glycerophosphate, $MnPO_3C_3H_7O_3$, is a white or reddish powder slightly soluble in water. It is prepared by the reaction of manganous hydroxide with glycerophosphoric acid and is used in medicine. A solution with citric acid is also sold.

Manganese linoleate or **manganous linoleate,** $Mn[O_2C(CH_2)_7CH{:}CHCH_2CH{:}CH(CH_2)_4CH_3]_2$, is a dark brown substance insoluble in water but soluble in hot linseed oil. It is obtained by boiling a soluble manganous salt with an aqueous solution of sodium linoleate. This manganese soap is sold as a 4 per cent liquid and as an 8.2 per cent solid based on the manganese oxide content. It is used as a drier in protective coatings.

Manganese resinate is a form of crude **manganese abietate,** $Mn(O_2CC_{19}H_{29})_2$, another manganese soap. The properties are similar to those of the linoleate but the precipitated grade is a light pink powder. A fused grade is produced by melting rosin with manganese oxide. The precipitated grade is obtained by boiling sodium abietate with a soluble manganous salt. The fused grade contains 3½ per cent of manganese oxide, the precipitated grade 7½ per cent. It is used as a drier in protective coatings.

Zinc, Zn, occurs in some ores as the sulfide and the carbonate. In both cases the zinc is associated with many other metals such as iron, cadmium, calcium, etc. Typical silicate minerals are **willemite,** Zn_2SiO_4, and **calamine,** $Zn_2SiO_4.H_2O$. The ore is ground and concentrated by flotation, then roasted with excess air to form the oxide. Zinc oxide is reduced to the free metal by heating with coal without access to oxygen. Since zinc is volatile, it is distilled over, condensed to a liquid and run into molds. It is a soft nontarnishing metal, soluble in acids and strong alkalies and is die-cast in the form of many alloys used for the production of small articles. Zinc-coating of iron produces **galvanized iron.** Such a coating is particularly valuable because zinc is chemically more active than iron. Therefore in case the coating becomes perforated further corrosion attacks the zinc rather than the iron. This is in contrast to the effect with tin-plated iron. Zinc is also used in dry batteries and in numerous other ways. Zinc compounds are generally white and, if soluble, are poisonous. While zinc also reacts as a negative element to form salts with basic elements such as sodium zincate, Na_2ZnO_2, none of these are of importance.

Zinc dust is a finely divided form of the metal, sold in various grades. By reaction with acid it is a powerful reducing agent and is sold as such for use in the synthetic organic chemical industry. To a minor extent it is used as a pigment. **Granular zinc** is a somewhat coarser form. When poured into water in the molten condition, zinc gives irregular flattened forms known as **mossy zinc.**

Zinc oxide, ZnO, is white, insoluble in water but soluble in acids. A naturally occurring form is **zincite.** It is obtained from ore as described under zinc, by heating zinc carbonate, or by oxidizing the vapor given off by boiling metallic zinc.

A U.S.P. grade, containing over 99 per cent of zinc oxide on ignition, is quoted and used in zinc oxide ointment, in other pharmaceuticals, and in cosmetics. Lead-free pigment grades are domestic American process and French process, green seal, red seal and white seal. Imported grades are gold seal, red seal, green seal and white seal. These vary in fineness, the gold seal being the finest. Many grades are quoted by well known trade names. Since zinc oxide can be obtained of extreme fineness and has an index of refraction substantially different from that of drying oils, it is a paint pigment of great importance. Such a difference in the index of refraction is essential to good covering power of a paint pigment. It is also used as a pigment in rubber goods, having valuable chemical properties in vulcanizing. It is used as a pigment in a multitude of other products such as in paper, printing ink, etc., and is a major ingredient of dental cements.

Leaded zinc oxide is a zinc oxide pigment containing varying quantities of lead sulfate. The usual grades quoted contain 5, 10, 35 and 50 per cent of lead sulfate. The use of these is largely confined to paint. **Zinc-iron oxide** is another pigment grade.

Zinc carbonate, $ZnCO_3$, is white and insoluble in water. It dissolves in acids, alkalies, ammonium salts and alcohol. It occurs naturally as the mineral **Smithsonite,** and is used for the preparation of other zinc salts. **Zinc basic carbonate, basic zinc carbonate or zinc subcarbonate,** $ZnCO_3.xZn(OH)_2$, where x is variable, is obtained by precipitating a solution of the sulfate or chloride with sodium carbonate. A U.S.P. precipitated powder and technical grade are quoted. The U.S.P. standard is from the 9th edition and calls for approximately $2ZnCO_3,Zn(OH)_2,xH_2O$, yielding at least 68 per cent of zinc oxide on ignition. Zinc carbonate is used as a pigment and rubber compounding ingredient, in ceramics, cosmetics, pharmaceuticals, and in medicine.

Zinc sulfate or **white vitriol,** $ZnSO_4,7H_2O$, is very soluble in water. It is prepared by the action of sulfuric acid on zinc or zinc oxide. An impure form is obtained by roasting a zinc sulfide ore at a low temperature. The salt is sold in crystalline, flake and powder forms. The U.S.P. standard calls for 55.86-58.63 per cent of the anhydrous salt, corresponding to not less than 99.5 per cent of the heptahydrate. Uses are for manufacture of other zinc salts, for preserving hides, as a mordant in printing cotton, in ceramics, in zinc-plating and for numerous miscellaneous purposes.

Zinc sulfide, ZnS,H_2O, is a white to yellow pigment insoluble in water but soluble in acids. It occurs in nature as **zincblende** or **sphalerite,** ZnS, and is prepared by treating a neutral solution of a zinc salt with hydrogen sulfide. Zinc sulfide is used as a high-quality pigment in paint, rubber, plastics, and other products, and as a base for color lakes.

Lithopone is a mixture of the chemically equivalent amounts of zinc sulfide and barium sulfate. It is white and insoluble in water. The manufacture is by mixing equivalent amounts of zinc sulfate and barium sulfide with water. The properties depend to an important degree on the subsequent roasting operations. Grades quoted are ordinary and high-strength. A grade containing titanium oxide is also quoted. As a pigment it does not darken on exposure to sulfides. The price is lower than that of zinc oxide. Uses as a pigment are varied, as in paint, leather, paper, rubber, etc. A corresponding orange to red cadmium compound is known as cadmium lithopone.

Zinc chloride, $ZnCl_2$, is a colorless hygroscopic salt, extremely soluble in water, alcohol or ether. It is obtained by heating zinc with dry chlorine gas, by the action of hydrochloric acid on zinc or zinc oxide, or by heating a mixture of zinc sulfate and sodium chloride. In concentrated solution, zinc chloride has a solvent action on starch and cellulose. The salt is sold in fused and granular grades, and in solution. A U.S.P. standard requires 95 per cent of zinc chloride. Uses are as a dehydrating agent, a catalyst, for preserving wood, as an antiseptic and disinfectant, as a sizing and weighting agent in the treatment of textiles, in adhesives, in making parchment paper, in dentifrices and in medicine.

Zinc ammonium chloride is a double salt of zinc chloride with ammonium chloride, of indefinite composition but sometimes classed as $ZnCl_2,3NH_4Cl$. It is used as a flux in soldering and welding, and in dry batteries.

Zinc iodide, ZnI_2, is extremely soluble in water and soluble in alcohol or ammonium carbonate solution. The solutions are unstable to light and air. It is prepared by the reaction of barium iodide with zinc sulfate. Barium sulfate precipitates and the filtrate is evaporated. It is used in medicine.

Zinc fluoride, ZnF_2, is a white powder insoluble in water or acids. It is produced by the reaction of sodium fluoride with zinc acetate or by dissolving zinc hydroxide in hydrofluoric acid. Uses are in making ceramic glazes, in impregnating lumber to improve resistance to decay and attack by animal organisms, and in galvanizing.

Zinc chromate or **zinc yellow** is a yellow pigment, a double salt of zinc chromate, $ZnCrO_4$, and potassium bichromate, $K_2Cr_2O_7$. It is of indefinite composition. The pigment is slightly soluble in water and is prepared by the reaction of potassium bichromate and a soluble zinc salt. The pigment is stable to hydrogen sulfide and is used in many products.

Zinc cyanide, $Zn(CN)_2$, is a white salt of zinc, soluble in dilute acids but not in water. It is prepared by the reaction of a soluble zinc salt and potassium cyanide. Uses are for zinc- and other metal-plating, and in pharmaceuticals.

Zinc arsenate has a variable composition approximating that of $5ZnO,2As_2O_5,4H_2O$. It is insoluble in water but soluble in acids or alkalies, and is prepared by the reaction of a solution of sodium arsenate and a soluble zinc salt such as the sulfate. It is poisonous and is used as an insecticide.

Zinc arsenite, $Zn(AsO_2)_2$, is similar to the arsenate in properties, preparation and use.

Zinc stearate is a very fine, soft and bulky amorphous powder. The formula, $Zn[O_2C(CH_2)_{16}CH_3]_2$, represents a purity never attained. It is insoluble in water but soluble in acids, and is prepared by the reaction of sodium stearate with a soluble zinc salt. U.S.P. and technical grades of precipitated material are sold. The U.S.P. grade is a mixture of zinc stearate and zinc palmitate containing 13-15.5 per cent of zinc oxide. It is used as a dusting powder, in face powder and cosmetics, and in various products where an organic salt of zinc is required.

Zinc palmitate is similar to zinc stearate but less bulky and not of as good quality. If pure the formula would be $Zn[O_2C(CH_2)_{14}CH_3]_2$. The method of preparation is similar to that of zinc stearate but the use is more limited, being largely as a flatting agent in lacquer.

Zinc resinate has only approximately the composition of **zinc abietate,** $Zn(O_2CC_{19}H_{29})_2$. It is the light brown product resulting from fusing rosin with zinc oxide. A precipitated grade results from boiling a solution containing sodium abietate and zinc sulfate. Both fused and precipitated grades are quoted for use as driers in protective coatings.

Zinc sulfocarbolate or **zinc phenolsulfonate,** $Zn(SO_3C_6H_4OH)_2 \cdot 8H_2O$, is a slightly soluble white powder which is prepared by heating zinc hydroxide with phenolsulfonic acid. The N.F. grade is used in pharmaceuticals, largely as an antiseptic.

CHAPTER XI

COMPOUNDS OF ALUMINUM, CHROMIUM AND IRON

Aluminum, Al, is a silvery, bluish, malleable metal. The spelling and pronunciation are sometimes that of **aluminium,** particularly in British literature. Aluminum is soluble in dilute hydrochloric acid and in hot alkaline solutions. Its compounds are very widely distributed, being next most common to oxygen and silicon. In spite of that, its quantity production as an element dates only from 1886. Since it is very reactive, the natural compounds are very stable, examples being clays and many precious stones. The commercial ore is **bauxite,** a hydrated oxide relatively free from iron. For production, purified bauxite, $Al_2O_3,2H_2O$, is dissolved in molten cryolite, a double fluoride $3NaF.AlF_3$, which may be obtained from natural sources or may be made synthetically. In the latter case, the mixture consists of $2AlF_3,6NaF,3CaF_2$. The cryolite is kept fused by passing an electric arc between carbon electrodes and the dissolved bauxite is decomposed by the electric current into aluminum and oxygen. Aluminum sinks to the bottom of the tank where it can be drawn off in the molten state, while the oxygen goes to the anode where it reacts with the carbon, so that the carbon anodes have to be renewed from time to time. Fresh bauxite is added at intervals and aluminum drawn off. The process is continuous since the loss of cryolite is relatively small.

Virgin aluminum is quoted as a 98-99 per cent grade. The impurities consist of iron and silicon with traces of nitrogen, copper, carbon and possibly zinc. It is usually alloyed with 4-8 per cent of copper to harden it. Varied forms are quoted, such as sheets, rods, etc. As **aluminum wire** it is more efficient than copper on a weight basis as a conductor of heat and electricity. Europe, particularly Germany, has made great progress in the use of such wire as an electrical conductor. The use of thin **aluminum foil** is expected to increase, important applications being as wrapping material and for heat insulation.

Aluminum is produced on such a large scale, and is so widely distributed, that it is a comparatively cheap metal, cheaper than tin for example. The metal is familiar to everyone because of its wide applicability. The cooking utensils and structural aluminum which one sees every day are not, however, the pure metal, but this metal covered with a thin coating of aluminum oxide. The metal always forms this coating on contact with air and the nearly transparent film of oxide protects the aluminum from further reaction. In a special form known as **anodized aluminum** the oxide film has been produced of greater thickness and is blue or green in color. In addition to its wide use for cooking utensils and as an architectural material, it has been applied as alloys in all sorts of industries where a light metal is of advantage, in airplane construction, in stream-lined trains, as parts of industrial machinery, for storage tanks and in electric equipment. An alloy containing 1 per cent of manganese is important in this field. A very strong aluminum alloy is known as **Duralumin,** which contains small amounts of copper, manganese and magnesium.

The compounds are practically all white and the salts are usually soluble in water. They are relatively inexpensive and therefore widely used. While **alumina** is properly a term for aluminum oxide the salts are often so called, alumina sulfate for example instead of aluminum sulfate.

Aluminum powder has been steadily increasing in applications as a pigment. Grades of powder quoted are extra fine lining; standard lining; ink; extra brilliant litho; extra fine litho; standard litho; wallpaper; rubber compounders; unpolished; extra brilliant varnish; extra fine varnish; standard varnish. Printing with aluminum-base ink is in common use. For many applications the aluminum powder contains up to 10 per cent of copper to give an improved brilliance and the powder is "polished" by coating with stearic acid. **Aluminum paste** is sold, which is aluminum powder ground in oil ready for further mixing in aluminum paints. Grades are extra fine lining paste, and standard. Because of its high reflective value it is widely used on exterior structures. Both **aluminum leaf** and copper-aluminum alloy leaf, under the name of **composition metal leaf** are also quoted.

Aluminum hydroxide, aluminum hydrate or **aluminum trihydrate,** $Al(OH)_3$, is white and insoluble in water but soluble in acids. Various hydrates occur in nature but are not suitable for the uses to which aluminum hydrate is applied. The compound is amphoteric and therefore behaves both as a base and an acid. It is prepared by fusing aluminum ore with soda ash or caustic soda, when a solution of sodium aluminate is obtained. This can be separated by filtration from impurities occurring in the ore. The hydroxide is precipitated from solution by rendering it approximately neutral. The product is sold as light, the pure grade, and a heavy grade precipitated on barium sulfate. The latter is of course much lower in price. The light grade is about 96 per cent pure. Aluminum hydrate is used as a special pigment, as a base for organic lakes and in special glasses. In many cases where aluminum hydrate is needed in a product it is manufactured in the process.

Aluminum sulfate, $Al_2(SO_4)_3,18H_2O$, is extremely soluble in water. An anhydrous form exists but is relatively unimportant. The aqueous solution is distinctly acid due to hydrolysis. The product is made by the reaction of sulfuric acid and bauxite or by the reaction of aluminum hydroxide with sulfuric acid. That obtained from the mineral is usually contaminated with iron. Both commercial and iron-free grades are quoted. It is used as a fireproofing agent, in water purification, as a mordant, as a clarifying agent by reaction in alkaline solution to precipitate gelatinous aluminum hydroxide, in sizing paper, for alum tannage of leather, for preparation of waterproofing materials, and for many other purposes. Trade terminology often refers to it as **alum** although correctly the alums are double salts. Where the use is for the aluminum content, aluminum sulfate is to be preferred to aluminum alums because of lower price and a higher proportion of aluminum content. In some special uses true alums are essential, and in others, their use is continued because of past favorable experience with them, instead of replacing them with a lesser weight of aluminum sulfate, which itself sells for a lower price per pound.

The true **alums** are hydrated double salts of sulfuric acid containing a univalent ion or a radical and a trivalent ion or radical, which may or may not be aluminum, combined with 24 molecules of water of hydration. Strictly speaking other elements may replace sulfur but this is of no commercial importance.

Potassium aluminum sulfate, potassium alum or **potash alum,** $K_2SO_4,Al_2(SO_4)_3,24H_2O$, was long called merely alum or **common alum** because it was the first known of this group of salts. It is soluble in cold water and very soluble in hot. Like the other aluminum alums it gives a slightly acid reaction in solution. It is largely obtained from **leucite,** a silicate mineral containing potassium and aluminum. The mineral is separated from the gangue, ground, treated with sulfuric acid and the alum recrystallized in the usual way. Granular, lump and powdered forms are sold. U.S.P. potassium alum contains not less than 99.5 per cent of the hydrated salt. U.S.P. burnt alum is the product obtained by quickly driving off the water of hydration by heat. The product is then porous and bulky, and contains not less than 96.5 per cent of the anhydrous salt. The uses are largely the same as for aluminum sulfate.

Ammonium aluminum sulfate, ammonium alum or **ammonia alum,** $(NH_4)_2SO_4.Al_2(SO_4)_3,24H_2O$, is similar in properties to potassium alum. Aluminous shale or bauxite is calcined and dissolved in sulfuric acid, together with by-product ammonia from the coal-gas industry. Iron is apt to be present as an impurity but it is largely removed by recrystallizing the alum from water. Commercial forms of ammonium alum are granular, lump, powdered and burnt. The U.S.P. grades of the hydrate and the anhydrous form meet the same standards set for the corresponding potassium compounds. Uses are similar to those of aluminum sulfate.

Sodium aluminum sulfate, sodium alum or **soda alum,** $Na_2SO_4,Al_2(SO_4)_3,24H_2O$, is similar to the other aluminum alums. Aluminum sulfate is obtained by the action of sulfuric acid on some natural source of aluminum. Sodium chloride is added to the solution and the alum formed separates on cooling. It is purified by recrystallization. Technical and crystalline grades are sold. It is used for much the same purposes as the aluminum sulfate and in addition is used as the acid ingredient in some types of baking powder.

Aluminum chloride must be considered as two different chemicals, one anhydrous and the other a hydrate. **Anhydrous aluminum chloride,** $AlCl_3$, is normally a yellow to greenish material. If pure it is white. The material absorbs moisture from the air, giving off hydrogen chloride gas. If added to water it reacts with explosive violence to form aluminum hydroxide or a basic chloride and give off hydrogen chloride. It is soluble in many organic solvents. Anhydrous aluminum chloride is made by heating aluminum with chlorine gas or hydrogen chloride or by calcining bauxite and heating with carbon and chlorine gas. Iron and silicon are the impurities most apt to be present. It is used as a reagent in synthetic organic chemistry and as a catalyst in oil cracking. The development of a large market for the latter purpose has radically reduced the price.

Hydrated aluminum chloride, $Al_2Cl_6,12H_2O$, is very soluble in water, alcohol or ether. The aqueous solution hydrolyzes to give an acid reaction. It is made by solution of bauxite or aluminum hydrate in hydrochloric acid. Grades are commercial crystals and a 32° Baumé solution. It is used for water purification, in printing dyestuffs and for miscellaneous purposes where the sulfate radical of aluminum sulfate would interfere.

Feldspar is a potassium or sodium aluminum silicate of somewhat indefinite composition. It is insoluble in water and substantially insoluble in acids. It may be white, flesh color, blue, or green. The usual composition approximates K_2O, $Al_2O_3,6SiO_2$. It is graded in the trade to over 17 per cent of combined aluminum oxide content. Silica will normally exceed 67-68 per cent. In **potash spar,** from 10-12 per cent of combined potassium oxide will be present, and in **soda spar** 9-10.5 per cent of combined sodium oxide. Potash spar contains some sodium oxide and soda spar some potassium oxide. The material is mined, classified and crushed. Grades quoted are enamel, 100 mesh; glass, 20 mesh; and pottery. As indicated from the grades, it is used as a chemical to furnish the aluminum content in glass and enamels and as a constituent part of pottery bodies. In addition, some is used as an abrasive in household cleaners and for other miscellaneous purposes. To a minor extent other aluminum compounds such as **pyrophyllite, nepheline syanite** and even talc, a magnesium silicate, compete in various applications.

Clay is a general term usually applied to a product because of physical rather than chemical properties. The materials so named are aluminum silicates of varying degrees of refinement. **China clay** or **kaolin** consists essentially of a hydrated aluminum silicate, contaminated with some finely divided quartz and mica, which may not be entirely removed during the washing process to which the naturally occurring material is subjected. The presence of quartz and mica introduces small amounts of iron, lime, magnesia and alkalis. Clay is found in England and in various parts of the United States. English clay is more plastic and whiter in color than most of the American kaolins. The clay is infusible, plastic when wet, and retains its white color at high temperatures. It is insoluble in water, acid or aqueous alkali but dissolves in fused alkalies. Domestic grades are dry-ground, air-floated 99.75 per cent through 300 mesh, and 99.75 per cent through 200 mesh; and water-ground, silk-bolted 99.9 per cent through 325 mesh. Imported grades are white, lump and powdered. China clay is used in making porcelain, tiles, and electrical insulators, and as a pigment and filler in paper, textiles, paint, rubber, etc.

Bentonite is a naturally occurring colloidal clay found in the western part of the United States. It swells greatly when wet with water. This swelling is promoted by various treatments such as admixture of magnesium hydroxide. Grades are 96 per cent through 300 mesh and 92 per cent through 200 mesh. It is used as a plasticizing agent as in pottery clay, as a bonding agent in chemical porcelain, pencil lead, molding sand, etc., as a dispersing agent in emulsions and suspensions, and as filler in rubber and other compounds.

Fuller's earth is a naturally occurring clay consisting largely of hydrous aluminum silicate. It somewhat resembles potter's clay but is lacking in plasticity and is highly adsorbent. The name originates in its use for fulling cloth, for which there is relatively little demand left. Domestic and imported grades are sold, of which the imported is much more expensive. It is used as a decolorizing agent, filtering medium and as a filler in varied products. Some grades are acid-treated to increase their efficiency as decolorizing agents.

Mica is the name of a class of minerals varying widely in composition and occurring in various parts of the world. Essentially they are silicates of aluminum and an alkali such as potassium, sodium or lithium. Iron, magnesium and chromium may be present, so that the product varies in color from transparent to gray, green, red, brown or black. The usual form occurs in very thin, more or less elastic leaves. Dry-ground grades are plastic, 40 mesh, 100 mesh, 140 mesh and roofing. Mica is used in paint and lacquer; wall or coated paper, and rubber. **Sheet mica** is also known and sold as rather large sheets for use as transparent windows to withstand heat, where glass will not serve.

Slate flour is a finely ground **slate,** a rock consisting of hydrous aluminum silicate with admixtures of many other minerals. It is colored gray, green and black by impurities. Uses are as an inexpensive filler where the color is not an objection.

Ultramarine blue is an insoluble, bright blue pigment of variable composition. It is sometimes called **imitation ultramarine blue,** since a natural blue ultramarine is known. It is prepared by roasting a mixture of kaolin, soda ash, sulfur and charcoal, and sometimes sodium sulfate and silica, and grinding the product to a powder. The dry pigment is sold in a jobbing grade, in many regular grades by number and letter, and in six special grades by number. Pulp ultramarine blue is sold in four grades by number. It is used as a paint pigment, in calico printing, in laundry blue, printing ink, for neutralizing the yellow color of paper, for coloring soaps, rubber, linoleum, plastics, etc.

Normal aluminum acetate, $Al(O_2CCH_3)_3$, is soluble in cold water but decomposed by hot water to give **basic aluminum acetate,** $Al(OH)(O_2CCH_3)_2$. The latter is insoluble in water but soluble in strong acids. The normal salt is more strongly hydrolyzed than other aluminum salts. It is made by the reaction of aluminum hydroxide with acetic acid and, because of its instability, the normal acetate is sold in C.P. 20 per cent solution. It is of particular value to the dyer as a mordant and in the preparation of lakes. It is also used as a waterproofing agent on textiles, and in embalming. The basic acetate has much the same uses as the normal acetate.

Aluminum stearate, $Al[O_2C(CH_2)_{16}CH_3]_3$, is a soap. It is a white to yellow amorphous powder, insoluble in water but soluble in turpentine or in petroleum solvents. It is produced by mixing solutions of a soluble aluminum salt and sodium stearate. The precipitated grade is available commercially and is used as a drier in protective coatings, a thickener for lubricating oils, as a waterproofing agent, and for producing gloss on varied products.

Aluminum oleate, $Al[O_2C(CH_2)_7CH:CH(CH_2)_7CH_3]_3$, is a soap similar to the stearate in properties, preparation and uses, except that it is a gelatinous mass rather than a dry solid.

Aluminum palmitate, $Al[O_2C(CH_2)_{14}CH_3]_3$, is another aluminum soap analagous to the stearate. It is a yellow to white amorphous solid.

Aluminum resinate is an impure **aluminum abietate,** $Al(O_2CC_{19}H_{29})_3$, a brown amorphous soap precipitated by reaction of soluble aluminum salts and sodium abietate. The properties and uses are similar to those of the stearate. A fused grade is also made by heating rosin with aluminum hydroxide, but the reaction is incomplete.

Chromium, Cr, is a bright, hard metal used as an alloying element, and in the pure form, as a plating material. The natural ore is largely **iron chromite,** $Fe(CrO_2)_2$. The metal is of major importance in chrome steel, which usually contains about 2 per cent, and in stainless steel or rustless iron, which usually contains about 14 per cent, as well as in alloys like nichrome, 60Ni, 15Cr, 25Fe.

Development of methods of plating from solutions of chromic acid revolutionized the plating industry within a comparatively few years. Nickel plating was largely replaced by chromium plating, which gives a brilliant, bluish-white, nontarnishing surface. Usually brass parts are first nickel- or copper-plated as a base for chromium plating.

Chromium is both acidic and basic in its properties. It is soluble in hydrochloric and sulfuric acids, but is made "passive" or nonreactive by nitric acid. Compounds such as sodium or potassium chromates or bichromates and chromic acid have already been discussed. Zinc chromate, known as zinc yellow, appears under zinc. Lead chromate or chrome yellow and the derived chrome greens appear under lead. When chromium is in the negative radical the compounds are usually yellow. In contrast to these the chromic salts are usually green, a color associated with the chromic ion. Chromous compounds also exist but are relatively unimportant.

Chromic oxide or **chrome oxide green,** Cr_2O_3, is insoluble in water but slightly soluble in acids. It is a medium green pigment obtained by heating dry ammonium bichromate, by heating chromium hydroxide, or by heating potassium bichromate with sulfur, and washing out the potassium sulfate. The oxide is offered as ordinary domestic; ceramic, standard grade; ceramic, light shades; and imported. It is used mainly in ceramics as a coloring agent. While used in paints, it is not to be confused with chrome green, which is a mixture of Prussian blue and lead chromate.

Chromic sulfate or **chromium sulfate,** $Cr_2(SO_4)_3.15H_2O$, is very soluble in water. A series of hydrates are formed but the 15-hydrate is the commercial one. The product is obtained by treating the hydroxide with sulfuric acid, and is offered in pearls, powder and scales. It is used as a mordant in dyeing, and for production of other chromium compounds. **Basic chromic sulfate** used in the tanning of hides, is usually produced in the tannery by reduction of the cheapest soluble chromium compound, sodium bichromate, with a cheap reducing agent, both for reasons of cost and to obtain the desired control of the degree of basicity.

Chrome alum, chrome potash alum or potash chrome alum, $K_2SO_4,Cr_2(SO_4)_3,24H_2O$, is one of the double salts called alums. It is prepared by crystalliation from the proper proportions of chromic sulfate and potassium sulfate, the alum being less soluble than either salt. This furnishes a means of purification. The violet-red crystals are used technically where high purity of the chromium salt is essential as in some mordanting and printing operations, and in the manufacture of inks. Occasionally it is used for tanning and other purposes in place of chromic sulfate. **Chrome ammonium alum** or **ammonium chrome alum,** $(NH_4)_2SO_4,Cr_2(SO_4)_3,24H_2O$, is similarly prepared and used.

Chromium fluoride, $CrF_3,4H_2O$, is a green powder. The water of hydration may vary. It is very soluble in cold water and soluble in alcohol. It is produced by solution of chromic oxide in hydrofluoric acid, and usually sold as a powder. Major uses are in the printing and dyeing of textiles and as a coloring for artificial and natural stone.

Chrome cake or **chrome saltcake.** See sodium sulfate.

Chromium acetate or **chrome acetate,** $Cr(O_2CCH_3)_3,H_2O$, is a soluble gray-green salt produced by the reaction of chromic hydroxide and acetic acid. It is quoted in somewhat impure form at 17.5 per cent of chromium; in a solution containing 8 per cent of chromium; and as a 20 degree Baumé solution. The major use is as a mordant in dyeing and printing textiles.

Chrome yellow: See lead chromate.

Chrome green: See lead chromate.

Chrome orange: See basic lead chromate.

Chromium trioxide: See chromic acid.

Iron, Fe, is a rather reactive metal, soluble in acids. While bright when exposed, oxidation to form an oxide occurs rather quickly. In a very thin layer this may be yellow or blue; in a thicker layer, black, but commonly it is red, brittle, and nonadherent, resulting in scaling and the further corrosion of exposed surfaces. This tendency to corrosion is largely due to the presence of substantial amounts of impurities. Iron is widely distributed, largely as the ferric oxide, **hematite.** The metal is obtained from this by smelting with coke and is further purified to produce steel. Typical iron contains carbon, 2-4.5 per cent; silicon 0.7-3 per cent; sulfur 0.1-0.3 per cent; phosphorus 0-3.0 per cent; and manganese 0.2-1 per cent. When cooled rapidly this is **white cast iron** which is brittle. Cooled slowly much of the carbon separates as graphite to give **gray cast iron** which is softer and tougher. In **wrought iron** slag inclusions occur and the structure is fibrous. This form is now of minor importance. In **steel** all impurities are reduced, but in particular carbon is only 0.5-2 per cent. The metallurgy is a matter of detailed technical art. Much is recovered from prior use as scrap metal.

Both ferrous or bivalent and ferric or trivalent compounds are important. The ferrous are usually green and the ferric red to brown. Iron as a negative radical is of no importance although ferrites and ferrates exist. Often the compounds are called iron salts such as iron chloride instead of ferric chloride, a practice which assumes that the user will be sufficiently familiar with the subject to know which is meant.

Reduced iron or **ferrum reductum** is a special form of finely divided metallic iron. It is soluble in acids but not in water or alkalies. This grade is produced from iron oxide by heating in a stream of hydrogen. The usual grade is 90 per cent. The U.S.P. grade contains not less than this. It is used with acid as a less powerful reducing agent than zinc dust.

Iron oxides have many forms and technical uses aside from serving as the principal ore of iron. **Magnetic iron oxide, black iron oxide** or **black rouge,** Fe_3O_4, is a natural ore, **magnetite.** The oxide is also produced synthetically. It is quoted as pure and as grades 1 and 2 of lower quality. Aside from metallurgical uses it serves as a very stable pigment. **Red iron oxide** or **red oxide** is the mineral, hematite, or a synthetic oxide. The latter is obtained by calcining ferrous sulfate. The color can be regulated by the conditions of calcination. By adding hydrated lime in calcination this is converted to calcium sulfate, and a diluted iron oxide obtained directly. Ferrous oxalate also gives the red oxide on decomposition by heat.

Persian red or **Persian gulf oxide** is a natural earth pigment which derives its name from the locality from which it was originally obtained, the land surrounding the Persian Gulf. It consists mainly of ferric oxide, and is also known as **Indian red.** It is quoted as pure and 80-85 per cent. **Spanish oxide** is another natural iron oxide. **Synthetic iron oxide** with or without extenders, added inert matter, is **rouge** or **crocus. Purple oxide** is a calcined iron pyrites. **Pure red oxide** is quoted of 80 or 85 per cent purity. **Tuscan oxide** or **Tuscan red** is an expensive form of oxide consisting of an iron oxide pigment used as a base for an organic lake of the para toner type. From 5 to 20 per cent of croceine, eosin, alizarin, etc., are often used for the purpose. Other names are too numerous even to list. These varied oxides are used as pigments in paint and rubber goods and numerous other products. Natural oxides mixed with wood shavings are used for the removal of sulfur compounds from gas. Manufactured grades are used as very fine abrasives.

Metallic red is an earth or ore which occurs naturally in Pennsylvania and which contains about 90 per cent of ferric oxide. The ground material is used in coloring bricks and in low-priced paint, as in roof paint. It is also sold under the name of **metallic brown,** although red in color. Under that name it may contain extenders, reducing the ferric oxide content to 50-70 per cent.

Brown iron oxide is a synthetic material precipitated from a mixture of ferrous sulfate and sodium carbonate, and sold for use as a pigment.

Turkey brown or **Turkey umber** is a natural earth which serves as a permanent pigment and which contains iron and manganese oxides, and some clay. It is used in paint.

Brown umber or **burnt umber** is a naturally occurring brown earth containing iron and manganese oxides and silica. Grades sold are American and Turkey umber. The latter comes from Cypress, is judged superior to the American product and commands a premium. Brown umber is used as a permanent pigment for ink, paint, etc. **Vandyke brown** is obtained from bog earth and contains iron oxide plus organic matter. It is used as a brown pigment.

Brown sienna is a naturally occurring amorphous product consisting mainly of hydrated iron oxide with some silicates and manganese oxide. **Raw sienna** is the natural material quoted in domestic and in numerous Italian grades. **Burnt sienna** produced by careful calcination has a deeper color and is similarly quoted. Both have varied uses as pigments.

Yellow iron oxide or **yellow umber** is a natural grade which is a mixture of hydrated iron oxides. As made synthetically ferrous hydroxide is precipitated from ferrous sulfate solution with lime or caustic soda or a mixture of the two, and oxidized by blowing with air. The synthetic grade therefore may contain more or less calcium sulfate according to the conditions of precipitation. Both natural and synthetic grades are quoted for various pigment uses.

Yellow ocher is a naturally occurring earthy material containing hydrated iron oxide and silicates. It varies in quality according to the depth of color and the amount of oil required as a vehicle. Several grades of American and French golden and yellow ocher are sold by letter designations for use as pigments.

Ferrous sulfate, green vitriol, or **copperas,** $FeSO_4,7H_2O$, is a greenish crystalline salt, often known as **iron sulfate** although there is also a ferric sulfate. It is very soluble in water. It may be obtained by allowing pyrites, FeS_2, to oxidize in contact with water. Practically, it is a by-product from pickling iron and steel, as in the tin plate and galvanizing industries, and is also produced by solution of detinned scrap or other grades of iron in dilute sulfuric acid. The crystals are obtained on evaporation. Crystalline and granular grades are sold. The U.S.P. grade contains 54.36-57.07 per cent of anhydrous ferrous sulfate, corresponding to not less than 99.5 per cent of the heptahydrate. It is a raw material for making iron oxide pigments, a cheap iron salt for clarification of water or industrial waste, and serves as a basis for making many other iron compounds.

Ferric sulfate, iron persulfate or **iron trisulfate,** $Fe_2(SO_4)_3$, usually contains about 5 molecules of water of hydration, and is a brown crystalline compound. Theoretically it exists as anhydrous or with 9 molecules of water. It is slightly soluble in water. A U.S.P. aqueous solution is sold containing 9.5-10.5 per cent of iron. It is used in dyeing, in etching aluminum, and in medicine.

Pyrites is an insoluble, yellow to brown, naturally occurring sulfide of iron expressed by the formula FeS_2. Small amounts of other metals are usually present, such as nickel, cobalt, copper, arsenic, silver, etc. It occurs in various parts of the world but the major deposits are in Spain. It is used in the manufacture of sulfuric acid and as an iron mineral. It is not to be confused with **ferrous sulfide,** FeS, a synthetic material used for the generation of hydrogen sulfide by reaction with dilute acids.

Ferric chloride, iron chloride, iron perchloride or **iron trichloride,** $FeCl_3,6H_2O$, is a very deliquescent yellow salt. It is extremely soluble in water and very soluble in alcohol, glycerine and ether. The usual commercial form is produced by passing chlorine into a solution of ferrous chloride and evaporating excess water, or by solution of an oxide or hydroxide of iron in hydrochloric acid. Technical and U.S.P. crystals, and a U.S.P. solution are sold. The latter contains 10-11 per cent as iron and 3-5 per cent of hydrochloric acid. A 40 degree Baumé solution is often quoted. Uses are as a dyestuff mordant, as an oxidizing agent, as a medicinal, and in general as a source of highly soluble ferric ion. **Anhydrous ferric chloride,** $FeCl_3$, also is known. It is obtained by the action of dry chlorine on red-hot iron, or by passing hydrochloric acid vapor over heated ferric oxide. Its properties are very similar to those of anhydrous aluminum chloride but of a lower degree of reactivity.

Ferrous iodide or **iron iodide** is a blue-gray, hygroscopic material, hydrated to approximately the composition $FeI_2, 3H_2O$. It is very soluble in water, soluble in alcohol and formed by the direct union of the elements, iodine and iron.

The latter is used in the form of filings to facilitate reaction. It is sold as a solid or in syrup form and is used for the formation of other iodides and in pharmaceuticals.

Ferric nitrate or **iron nitrate,** $Fe(NO_3)_3,9H_2O$, is a gray to violet deliquescent salt, very soluble in water and soluble in alcohol. It is produced by dissolving scrap iron in concentrated nitric acid and crystallizing. The commercial grade is used as a mordant.

Iron phosphate is used in both the ferric and ferrous forms. **Ferric phosphate,** $FePO_4,4H_2O$, is a yellowish-white powder, insoluble in water but soluble in acids. It occurs naturally as a mineral and is also obtained by the reaction of trisodium orthophosphate and ferric chloride. A medicinal product sold under the same name is water-soluble and contains sodium citrate. This is a characteristic property of various ferric phosphates, insolubility in water but solubility in solutions of salts of organic hydroxy acids. Scale and pearl forms are sold for use in medicine. **Ferrous phosphate,** $Fe_3(PO_4)_2,8H_2O$, is a grayish-blue powder, soluble in mineral acids but insoluble in water. It occurs as a mineral, is produced by the reaction of ferrous sulfate with trisodium phosphate, and is used in medicine.

Ferric pyrophosphate or **iron pyrophosphate,** $Fe_4 (P_2O_7)_3$, is a yellowish-white powder, soluble in acids and organic salt solutions but not in water. It is formed by the reaction of a soluble ferric salt with pyrophosphoric acid or of ferric citrate and tetrasodium pyrophosphate. Scale and pearl forms are sold for use in medicine.

Ferric hypophosphite or **iron hypophosphite,** $Fe(H_2PO_2)_3$, is a grayish-white powder, almost insoluble in water but soluble in solutions of citrates. It is formed by the reaction of hypophosphorous acid and ferrous carbonate with air oxidation or by reaction of an alkali hypophosphite and ferric chloride, and is used in medicine.

Ferric glycerophosphate or **iron glycerophosphate** is approximately $Fe_2[PO_4C_3H_5(OH)_2]_3$, prepared by methods analagous to the other glycerophosphates, and is sold in the form of a powder or yellow to green scales. It is very soluble in water and is used medicinally for correction of iron and phosphate deficiency in the diet.

Prussian blue is mainly ferric ferrocyanide $Fe_4[Fe(CN)_6]_3$, but contains some sodium and may contain potassium. The intense blue pigment is insoluble in water but soluble in acids and alkalies with decomposition. It is amorphous and is produced by precipitating a solution of a ferrous salt with sodium ferrocyanide. The precipitate of ferrous ferrocyanide, which is nearly white, is oxidized with a common oxidizing agent such as sodium bichromate and sulfuric acid, to form ferric ferrocyanide. Alternatively the ferrous salt may be oxidized to the ferric salt before precipitating. Several varieties of Prussian blue are sold, made by slightly different methods of manufacture, but essentially the same chemically. **Bronze blue** has a greenish and bronze undertone. **Celestial blue** is a Prussian blue reduced with 80-90 per cent of barytes. **Chinese blue** is similar to bronze blue and has a greenish undertone. **Milori blue** is greenish and brighter than bronze blue. These products differ slightly from each other because of differences in the method of manufacture. **Peacock blue** or **permanent blue** are terms for Prussian blues treated with phosphotungstic acid to give greater stability, particularly to light. **Soluble blue** is made by sedimenting Prussian blue as a pulp, working in oxalic acid or ammonium oxalate and drying. It then disperses readily in water. These pigments are available in dry form, or often as pulp. They are used for coloring where acid and alkaline sensitivity will not destroy them, as in paints, ink, match heads, etc. Soluble Prussian blue is used for laundry blue in the home but not in commercial laundries. Prussian blue combined with chrome yellow gives chrome green, as discussed under lead chromate.

Potash blue is related to Prussian blue. It is a class of pigment made by mixing potassium ferrocyanide and ferrous sulfate and oxidizing the resulting ferrous ferrocyanide. The final product contains some potassium. It is largely used in making carbon paper.

Ferric acetate or **iron acetate,** $Fe_2(O_2CCH_3)_6$, cannot readily be obtained as a solid but is available as an aqueous solution. In drying, insoluble **basic ferric acetate,** $Fe(OH)(O_2CCH_3)_2$, is obtained instead of the normal acetate. The latter is produced by the action of excess acetic acid on ferric hydroxide. The commercial grade is N. F. IV and contains about 31 per cent of anhydrous ferric acetate. A 17 degree Baumé solution is also quoted. It is used medicinally and to form the basic acetate as a mordant.

Ferrous oxalate or **iron oxalate,** $FeC_2O_4,2H_2O$, is obtained in the form of pale yellow crystals almost insoluble in water but soluble in acids. It is precipitated from a solution of a soluble ferrous salt and sodium oxalate. Scale and powdered forms are sold for use in photography and in the related blueprinting art, where minor differences in composition are important. These differences give rise to a large number of nearly similar iron salts.

Ferric sodium oxalate or **iron soda oxalate,** $2[Na_3Fe(C_2O_4)_3],9H_2O$, is an emerald-green crystalline salt, very soluble in water. It is formed by the reaction of sodium acid oxalate and ferric hydroxide and is used in photography and blueprinting. **Ferric oxalate** $Fe_2(C_2O_4)_3$, is not as stable nor as satisfactory.

Ferric potassium oxalate or **iron potash oxalate,** $2[K_3Fe(C_2O_4)_3],9H_2O$, is similarly prepared and has properties and uses similar to the corresponding ferric sodium compound.

Ferric ammonium oxalate or **iron ammonia oxalate,** $(NH_4)_3Fe(C_2O_4)_3,4H_2O$, consists of very soluble green crystals produced by the reaction of ammonium acid oxalate and ferric hydroxide. A crystalline grade is sold for use in the preparation of blueprint paper.

Ferric citrate or **iron citrate,** $FeC_6H_5O_7,3H_2O$, is a garnet-red compound nearly insoluble in cold water but soluble in hot. It is produced by the reaction of ferric hydroxide with citric acid. The U.S.P. VIII grade is sold in scale, pearl and powdered forms, containing not less than 16 per cent of iron. It is used in making blue-print paper, and like many other iron salts as a medicine.

Ferric ammonium citrate or **iron ammonia citrate** results from the reaction of ferric hydroxide with citric acid, followed by addition of the proper amount of ammonium hydroxide. The composition is indefinite. Brown and green grades are sold in scale, granular and pearl form. It is administered as medicine for its iron content and is used in the preparation of blue-print paper.

CHAPTER XII

ARSENIC, ANTIMONY AND TIN

Arsenic, As, occurs to such an extent in minerals refined for other values that there is a potential supply much larger than the demand. It is usually recovered as a by-product from the smelting of cobalt, nickel, copper and other ores, as the so-called white arsenic, which is the anhydride of arsenious acid and which has been discussed under that heading in the chapter on acids. The metal is obtained by reduction of the oxide and is a gray to black solid, usually crystalline but sometimes amorphous. The metal is insoluble in water but soluble under oxidizing conditions as in nitric acid or chlorine-water. While all soluble arsenic compounds are poisonous, the metal is not because of its insolubility. It is used to a small extent as an alloying material in lead but as an element is relatively unimportant. Arsenic occurs more as a negative or acid-forming than as a positive or basic element. Therefore its salts, such as sodium or potassium arsenite and arsenate, as well as others, are described with the proper positive element. Paris green is an important copper salt of arsenic.

Arsenic bisulfide or **red arsenic,** As_2S_2, is soluble in alkalies but not in water and occurs naturally in reddish-orange prisms as **realgar** or **orpiment.** It is also manufactured by subliming from a mixture of iron pyrites and arsenical pyrites and is used as a pigment and in pyrotechnics.

Arsenious chloride or **arsenic trichloride,** $AsCl_3$, is a colorless, fuming, oily liquid which decomposes on contact with much water to form arsenious acid and liberate hydrogen chloride. It can exist in dilute solution in concentrated hydrochloric acid, and is soluble in alcohol, ether and many other anhydrous organic solvents. Arsenic chloride is produced by the direct union of arsenic with chlorine, or in solution by distilling arsenious oxide with concentrated hydrochloric acid. It is used as a reagent in the synthetic manufacture of organic chemicals, including poisonous war gases. The use is limited by its high price. Hydrates analagous to those of aluminum and ferric chlorides do not exist.

Arsenious iodide or **arsenic triiodide,** AsI_3, is an orange-red powder soluble in water, alcohol, ether and other organic solvents. It is obtained by the direct union of arsenic with iodine and is used in medicine. The U.S.P. grade contains not less than 99 per cent of the salt.

Antimony, Sb, is a gray metal which occurs naturally as the sulfide, Sb_2S_3, called **stibnite.** This is reduced to the element, which is insoluble in water, but soluble in hot concentrated sulfuric acid. Major uses as a metal are in hard lead, which contains 15 per cent of antimony, and in type metal. Domestic and Chinese grades are quoted. While antimony enters into the negative radical of salts, these are unimportant. Some of the compounds in which it is a positive element are widely used. In general they are white, the sulfides being exceptions, and if soluble in water are poisonous. Some of the salts require the presence of acid to prevent formation of an insoluble basic salt.

Antimony trioxide or **antimony oxide,** Sb_2O_3, is the usual form of white oxide, insoluble in water but soluble in acids or alkalies. It is an acidic oxide but none of its salts as an acid are important. Preparation is by oxidizing antimony with dilute nitric acid, by burning antimony in the presence of a limited amount of oxygen, or by decomposing antimony trichloride with an aqueous solution of sodium carbonate. Domestic and imported grades are quoted. As **white antimony pigment** it enters the market in varied grades of 96-99.5 per cent purity, usually containing some sulfate and even sulfide. Aside from pigment use, antimony oxide is a basis for the manufacture of antimony salts.

Antimony sulfide or **antimony trisulfide,** Sb_2S_3, is insoluble in water but soluble in alkalies. It occurs in two forms. As found in nature it is a black crystalline substance. When precipitated from solutions of antimony salts, it is an orange-red powder. The latter turns black on being heated to 200° C. This sulfide is also known as **antimony needles.** It is used in making matches, in ruby glass, in refining gold and as a pigment. **Golden antimony sulfide** is a mixture of Sb_2S_5 with some free sulfur. The amount of sulfur may vary from 1 to 40 per cent. It is precipitated from sodium antimonate by soluble sulfides and is used primarily as a rubber pigment. This form of antimony sulfide varies in color from light orange to deep red. It is suitable for use in rubber because it is normally free from copper and manganese, which are present as impurities in practically all natural earth pigments and many synthetic ones. Absence of copper and manganese is essential to avoid deterioration of the rubber.

Antimony trichloride or **butter of antimony,** $SbCl_3$, is a soft, white to yellow, deliquescent material extremely soluble in water and soluble in alcohol and many other organic solvents. It is obtained by burning metallic antimony in chlorine; by dissolving antimony trisulfide in hydrochloric acid followed by distillation; or by distilling antimony with excess of mercuric chloride. The soft crystals react readily with an excess of water to liberate hydrochloric acid and to form **antimony oxychloride,** SbOCl, which is insoluble. Both the domestic and imported product are sold in the form of a solution of antimony trichloride. The crystalline form is also available. Antimony trichloride is used as a bronzing solution for iron, such as on gun barrels, for coloring other metals, in the preparation of other antimony salts, in dyeing, in plating and in medicine.

Antimony salt is a trade term for a mixture containing antimony fluoride and sodium fluoride. It sometimes contains ammonium sulfate in place of the sodium fluoride. It is also called **de Haens salt** and is used as a mordant in dyeing and printing textiles.

Antimony potassium tartrate or **tartar emetic** occurs as $K(SbO)C_4H_4O_6.\frac{1}{2}H_2O$, colorless or white crystals, soluble in cold water, very soluble in hot water and soluble in glycerine. It is prepared by heating antimony trioxide with potassium bitartrate in aqueous solution. The U.S.P. grade is in powdered form, having a content of not less than 99 per cent of the salt of the formula above. A technical grade is sold as crystals and as powder. The salt is used as a mordant in dyeing, and in medicine.

Tin, Sn, is a bright metal which is more important as the metal than in the form of its salts. Tin is soluble in mineral acids. The principal ore is **cassiterite,** which contains a large proportion of stannic oxide, SnO_2. The ore is pulverized and washed to remove foreign substances such as granite and slate. It is next roasted to drive off arsenic and change iron and copper sulfides to the oxide and sulfate respectively. After further washing to remove these, the oxide of tin is reduced with carbon, and cast. From its physical form the pure metal is often referred to as **block tin.** The usual grade is Straits, indicating its origin.

Since it does not react readily with organic acids, it is widely used for plating containers for the food industry. Thus a **tin can** consists of tin-coated iron; the metallic tin would not have adequate strength. The protection which it gives to the iron underneath is limited by the fact that tin is less active than iron. Therefore in case of a break in the coating, corrosion attacks the iron and perforation of the can may result. For this reason many tin cans containing acid foods are lined with lacquer or resinoid as an additional protection. Many items are marketed in tin tubes which are made of an alloy hardened with 0.5-5.0 per cent of copper. The malleability of tin permits it to be rolled into thin foil useful as wrapping for small items, mainly food products. Tin is used in many alloys of which the following are illustrative: **Babbitt metal,** Sn 90, Sb 7, Cu 3; **solder,** many formulas, such as Sn 50, Pb 50; **pewter,** Sn 80, Pb 20; **type metal,** many formulas, such as Pb 82, Sb 15, Sn 3; **white metal,** Pb 75, Sn 24, Cu 1; **bronze,** Cu 80, Sn 15, Zn 5; **gunmetal,** Cu 90, Sn 10. The salts are normally white and poisonous. Both bivalent and tetravalent compounds exist and some of each class are used industrially.

Stannic oxide or **tin oxide,** SnO_2, is white, insoluble in water but soluble in concentrated sulfuric acid. The crude cassiterite ore can be purified from iron and copper minerals. A pure form is obtained by burning tin in excess air. It is also often produced in hydrated form by precipitation from solutions of stannic salts, in which case it is known as **stannic acid,** or **metastannic acid,** H_2SnO_3. Aside from use in forming tin salts the oxide is precipitated on silk as a weighting agent, and on fabrics as a fire-retarding agent. It is used as a fine polishing agent and as an ingredient of special types of glass. Since tin is fundamentally a high-priced metal the oxide is used only where less expensive substitutes cannot replace it. Stannic oxide is not to be confused with the black **stannous oxide,** SnO, which is unimportant industrially.

Stannous chloride, tin crystals, or **tin salt,** $SnCl_2,2H_2O$, is extremely soluble in water and soluble in alkalies or in alcohol. It is formed by solution of tin in hydrochloric acid. The aqueous solution is unstable, being oxidized by air to stannic forms, unless excess of hydrochloric acid and crystals of metallic tin are present. The solid white crystals are the commercial form. Stannous chloride is used as a powerful reducing agent in synthetic organic chemistry, as a mordant in dyeing and printing textiles, as a discharge in textile printing, in the glass-silvering art and for numerous miscellaneous purposes.

Stannic chloride or **tin tetrachloride,** $SnCl_4$, is a colorless liquid which fumes in the air. It is soluble in alcohol or other anhydrous organic solvents. Cold water almost completely hydrolyzes it, but the stannic acid formed remains in colloidal suspension. It is decomposed by hot water. Crystalline hydrates are readily formed from the anhydrous material with small amounts of water. Stannic chloride is produced by passing dry chlorine over tin granules and distilling the colorless liquid, stannic chloride. Some of the solid product of commerce is a complex compound, Na_2SnCl_6,H_2O. The product is used in synthetic organic chemical reactions and in the textile industry.

CHAPTER XIII

COPPER, CADMIUM AND BISMUTH

Copper, Cu, is a red metal of characteristic color. Copper is not active enough to displace hydrogen from acids, but is soluble in oxidizing acids such as nitric or hot concentrated sulfuric acid. The varied ores are complex oxides and sulfides, such as **copper pyrites,** $CuFeS_2$, **chalcocite,** Cu_2S, and **cuprite,** Cu_2O. The metal also occurs in the free state. The major production is from sulfide ores by concentrating, roasting, forming copper matte, containing mainly iron and copper sulfides, reducing the matte to crude or **blister copper** and refining the latter electrolytically. Recovery of gold and silver in the last step pays for the electrolytic refining. Much copper is recovered as secondary metal from prior use. Electrolytic copper is the standard grade of commerce.

Copper is important as a good conductor of heat and electricity and is therefore preferred in electrical equipment to aluminum because of its lesser bulk. It is used for alloying with other metals. Many **brasses** are used, of which 60-90 parts of copper and 10-40 of zinc represents a range of compositions. Some tin is often added. Other alloys are **aluminum bronze,** 90 Cu, 10 Al; **German silver,** 52-60 Cu, 25 Zn, 15-22 Ni; etc. Alloys high in copper are used for industrial equipment such as kettles and evaporating pans. Other alloys are used for marine fittings, gun parts, mine equipment, etc.

Copper forms two series of salts, cuprous or monovalent and cupric or bivalent. The latter are the important group but numerous chemical applications depend on the change in valence. All of the soluble salts of copper are poisonous.

Gold bronze powder or **aluminum bronze powder** is essentially a yellow alloy of copper and aluminum, although small amounts of iron, manganese and tin may also be present. The alloy as originally produced contained 90 per cent of copper and 10 per cent of aluminum, but smaller proportions of aluminum may also be used. More than 11 per cent of aluminum causes the alloy to become too brittle. It is offered as powder which has usually been "polished" by coating with stearic acid. Typical grades are litho, moulding, printing-ink and radiator, varying greatly in degrees of fineness and in price.

Copper oxide exists in both in cupric and cuprous states. **Cupric oxide** or **black copper oxide** is insoluble in water but soluble in acids. It occurs naturally, but the pure grade is made by gentle ignition of the nitrate, carbonate or hydroxide. A special wire form is as short pieces of copper wire with a surface coating of oxide. Cupric oxide has varied uses such as to color ceramic materials blue or green, as a mild oxidizing agent, as a catalyst and for production of copper salts.

Cuprous oxide or **red copper oxide,** Cu_2O, is insoluble in water but soluble in acids, ammonium hydroxide, and ammonium salt solutions. It occurs naturally and is prepared by the controlled heating of copper wire, by the atmospheric oxidation of copper reduced in hydrogen or by reducing an alkaline copper solution with sugar. A commercial 50-75 per cent grade is sold. It is used to color glass ruby-red, to color ceramics, and as a mild reducing agent.

Cupric carbonate, copper carbonate or **basic cupric carbonate** is a dark green to blue powder soluble in acids but insoluble in water. It has a composition which may approach $Cu_2(OH)_2CO_3$. The product is obtained when a soluble carbonate such as sodium carbonate is added to a soluble cupric salt such as copper sulfate. The normal carbonate does not exist. Grades quoted contain 52-54 per cent and 18-20 per cent of cupric oxide. The compound is used as a pigment in making other copper salts, in insecticides and in pyrotechnics. This is the much prized **patina** present on bronze statuary and roofs after long exposure to the weather.

Copper sulfate, cupric sulfate, blue vitriol or **bluestone,** $CuSO_4.5H_2O$, is a blue crystalline compound which is by far the most commonly used copper salt. It also forms a white anhydrous salt, $CuSO_4$, and a light blue monohydrate. All are soluble in cold water and very soluble in hot. The pentahydrate is prepared by the oxidation of copper ores containing the sulfide, or by dissolving cupric oxide in dilute sulfuric acid. It hydrolyzes in aqueous solution to give an acid reaction. The usual technical grade is normally of better than 99 per cent purity, the usual impurities being iron and aluminum. The U.S.P. salt contains 63-66.8 per cent of anhydrous copper sulfate, corresponding to not less than 98.5 per cent of the pentahydrate. The monohydrate is also sold. Copper sulfate is used as a mordant, in copper-plating, in electric batteries, in germicides and insecticides, in pigments, in the leather industry, for the production of other copper salts, as a wood preservative, in engraving, and to destroy algae in drinking water. A mixture of copper sulfate solution and milk of lime is known and sold as **Bordeaux mixture,** a common agricultural insecticide.

Cupric chloride or **copper chloride,** $CuCl_2,2H_2O$, is a light blue crystalline compound extremely soluble in water. The anhydrous form is yellow. Cupric chloride is obtained by dissolving cupric oxide in an excess of hydrochloric acid. The salt hydrolyzes to give an acid reaction. It is used as a mordant, as a disinfectant, in metal refining, as a catalyst, as a preservative for wood, in photography and in water purification.

Cuprous iodide or **copper iodide,** CuI, is a brown to white powder insoluble in water or acids, except hydrochloric, but soluble in ammonium hydroxide and in potassium cyanide solution. It is obtained by the spontaneous decomposition of cupric iodide, which is formed by adding a soluble iodide to a cupric salt. Iodine is liberated. The material has medicinal uses.

Cupric nitrate or **copper nitrate,** $Cu(NO_3)_2,6H_2O$, is a blue deliquescent salt soluble in alcohol and extremely soluble in water. It also exists as a trihydrate, $Cu(NO_3)_2,3H_2O$. Cupric nitrate is produced by solution of copper or cupric oxide in nitric acid, and is used in photographic emulsions, insecticides, electroplating, the coloring of metals, as a mordant in dyeing textiles and for other miscellaneous purposes.

Cuprous cyanide or **copper cyanide,** $Cu_2(CN)_2$, is a white powder insoluble in water but soluble in hydrochloric acid, ammonium hydroxide and in potassium cyanide solution. It is formed by the spontaneous decomposition of cupric cyanide. The latter is formed momentarily by the reaction of potassium cyanide and a cupric salt. Copper cyanide is very poisonous. The technical grade is sold for use in electroplating.

Cupric acetoarsenite, or **Paris green,** is the complex salt obtained by boiling basic cupric acetate with arsenic trioxide. The composition is approximately $Cu(O_2CCH_3)_2,3CuAs_2O_4$. It is insoluble in water but soluble in acids or ammonium hydroxide. The green powder is used as an agricultural insecticide and fungicide and in the preservation of wood. Its limited use as a pigment is declining because of its poisonous nature.

Basic copper acetate or **verdigris** is formed by the action of acetic acid on copper. It is nearly insoluble in water but soluble in acids. There are varying formulas such as a green variety, essentially $2Cu(O_2CCH_3)_2,CuO$, and a blue variety, essentially $Cu(O_2CCH_3)_2,CuO$. The products are used as pigments, for dyeing and printing calico, and as wood preservatives.

Cupric stearate or **copper stearate,** $Cu[O_2C(CH_2)_{16}CH_3]_2$, is a copper soap, a light blue amorphous powder insoluble in water but soluble in most organic solvents except alcohol. It is obtained by heating copper sulfate solution with sodium stearate solution. The precipitated material is used in anti-fouling paint and for bronzing.

Cupric oleate or **copper oleate,** $Cu[O_2C(CH_2)_7CH{:}CH(CH_2)_7CH_3]_2$, is a soap which exists as a blue-green mass. It is insoluble in water but soluble in most organic solvents except alcohol. The oleate is obtained by the reaction of a solution of copper sulfate with a solution of sodium oleate. The precipitated grade is sold for preserving fish nets and lines, and for use as a drier in protective coatings such as paints.

Cupric resinate or **copper resinate,** $Cu(O_2CC_{19}H_{29})_2$, is another copper soap. It occurs as an amorphous blue powder with solubilities similar to those of other copper soaps. The resinate is made by heating copper sulfate solution with a solution of rosin soap. The precipitated grade is used as an insecticide and in anti-fouling paints.

Copper phthalocyanine blue is a complex blue pigment belonging to the organic class, although, as the name indicates, it contains copper. The product appears in two forms, one full-strength and one with less strength but more readily ground. Copper phthalocyanine is extremely stable to light and heat and is nonbleeding and nonreactive to vehicles. It has been described as the nearest approach to a perfect color material. It is used in paint and in printing inks, but is rather expensive.

Cadmium, Cd, is a silvery metal, insoluble in water but soluble in acids and some ammonium salt solutions. It occurs in association with zinc in ores, generally to the extent of about 0.5 per cent of the amount of zinc. Cadmium is recovered from the first fraction which collects when zinc is distilled. By repeated redistillation in the presence of carbon, purified cadmium is obtained. As a metal it is important for electroplating. It is also an ingredient of many alloys, although not in those used in large tonnage. The metal has minor uses. Some of its compounds are important pigments.

Cadmium sulfide or **cadmium yellow,** CdS, is a yellow pigment, insoluble except in concentrated acids. It occurs naturally as **greenockite.** Usually it is prepared by precipitation from acid solutions of soluble cadmium salts with hydrogen sulfide. It is used as a pigment in various media, as in paints, soap, printing ink, paper, rubber and in ceramic glazes. The yellow color is not changed by hydrogen sulfide.

Cadmium lithopone is the insoluble mixture of barium sulfate and cadmium sulfide analagous to ordinary lithopone which is the corresponding zinc product. It is made by mixing solutions of cadmium sulfate and barium sulfide, filtering, calcining, etc., and is available in varied colors such as golden, yellow, orange, and primrose. It is used as a pigment for the same purposes as cadmium sulfide and is to be visualized as a "let-down" grade of cadmium sulfide having greater tinctorial power than would result from ordinary physical admixture of the ingredients.

Cadmium red is a complex sulfide-selenide pigment. It is prepared from a mixture of 80-90 per cent of cadmium sulfide and 10-20 per cent of selenium. The mixture is heated to 700° C. Shades are light, medium light, medium, medium deep and maroon. They are fairly expensive.

Cadmium selenide is prepared in a reasonably pure form and is orange red. Methods of preparation are closely related to those for cadmium red and uses are similar. **Cadmium orange** is a "let-down" form of impure cadmium selenide.

Cadmium bromide, $CdBr_2$, consists of white to yellow crystals, is very soluble in water or alcohol, and soluble in ether. It is prepared by heating cadmium in bromine vapor for use in photography and engraving.

Cadmium iodide, CdI_2, is white and is similar to the bromide but even more soluble. It is obtained by treating cadmium oxide with hydriodic acid and is used in photography and engraving.

Bismuth, Bi, has the bright appearance usually associated with metals. It has a slight red tinge, is hard and brittle, and dissolves in hot concentrated nitric and sulfuric acids. It occurs chiefly free but also as the sulfide, **bismuth glance,** Bi_2S_3, and **bismuth ochre,** Bi_2O_3. Commercial requirements are largely filled by that recovered as a by-product from tin ores and during the refining of copper and lead. The oxide is reduced with carbon, with or without the use of a flux such as fluorspar, soda or lime. In some cases the metal is obtained by extraction with acid and reduced by heating the compound obtained with carbon and soda ash. The crude metal is usually contaminated with lead, iron, arsenic, sulfur, nickel, cobalt, antimony, copper, etc., and sometimes with silver and gold. Bismuth is one of the few substances which expand on solidifying, a property which it imparts to a number of alloys. Its thermal conductivity is the lowest of any metal, its melting point relatively low. In alloys it gives very easily fusible materials. For this reason it is used to form low-melting alloys suitable for plugs in sprinkler systems. Applications are limited by the relatively high price.

The compounds are in general white to light yellow. When weakly acid solutions of its salts are diluted, an insoluble basic salt is usually precipitated. These are called "sub," "oxy" or "basic" salts. The major uses of the salts are for medicinal purposes.

Bismuth trioxide or **bismuth oxide,** Bi_2O_3, is a heavy yellow powder, insoluble in water but soluble in acids. It is obtained by igniting bismuth nitrate, carbonate or hydroxide, and also occurs naturally. Uses are in medicine and for the preparation of other bismuth salts.

Bismuth hydroxide or **bismuth hydrate,** $Bi(OH)_3$, is a white to yellowish-white powder, soluble in acids but not in water. It is obtained as a white precipitate by treating a solution of a bismuth salt with a solution of caustic soda. A partially dehydrated compound, $BiO(OH)$, is produced by pouring bismuth nitrate solution into ammonium hydroxide solution. Both are used in medicine.

Bismuth chloride or **bismuth trichloride,** $BiCl_3$, is a yellowish-white crystalline material. While insoluble in water due to formation of the subchloride, it is very soluble in dilute acids and dissolves in absolute alcohol. The chloride is obtained by burning bismuth in an excess of chlorine or by treating metallic bismuth with hydrochloric acid. It is used for the preparation of other bismuth compounds.

Bismuth subcarbonate or **basic bismuth carbonate,** $(Bi_2O_2CO_3)_2,H_2O$, is a yellowish-white powder, soluble in acids but not in water. No normal carbonate is obtainable. The basic carbonate is prepared by adding a solution of a bismuth salt to a solution of ammonium carbonate. Ordinary X-ray and U.S.P. grades are sold to contain not less than 90 per cent of Bi_2O_3. It is used in medicine, in making other bismuth compounds and in X-ray work as a dense material to show the form and position of gastrointestinal organs.

Bismuth oxychloride or **bismuth subchloride,** $BiOCl$, is a white powder insoluble in water but soluble in mineral acids. It is precipitated by dilution of a slightly acid solution of bismuth chloride with water and is used as a pigment, in face powder and in medicine.

Bismuth oxyiodide or **bismuth subiodide,** $BiOI$, is a brick-red powder, insoluble in water but soluble in mineral acids.

It is prepared by methods analagous to those for the oxychloride, for medicinal use.

Bismuth nitrate, $Bi(NO_3)_3{,}5H_2O$, consists of colorless, deliquescent crystals. It is decomposed by water to the subnitrate but is soluble in dilute mineral acids, alcohol or acetone. The nitrate is obtained by evaporating a nitric acid solution of bismuth to dryness. It is used in the preparation of other bismuth salts, in luminescent pigments and in medicinals.

Bismuth subnitrate, bismuth oxynitrate or **basic bismuth nitrate,** $BiONO_3{,}H_2O$, is a white powder insoluble in water but soluble in acids. The formula is only approximate. The U.S.P. grade contains not less than 79 per cent of bismuth trioxide. The salt results from the dilution of a slightly acid solution of bismuth nitrate with water. It is used in cosmetics, ceramics, and in medicine, and is probably the most used bismuth compound.

Bismuth citrate, $BiC_6H_5O_7$, is a white powder insoluble in acids or water but soluble in ammonium citrate solution. It results from boiling bismuth subnitrate with a solution of citric acid. The usual grade is U.S.P. VIII, which yields 56-58 per cent of bismuth trioxide. The use is mainly medicinal.

Bismuth ammonium citrate is a white powder of variable composition which is easily soluble in water. It is prepared by the reaction of bismuth subnitrate, citric acid and ammonium hydroxide, for use in medicine.

Bismuth subbenzoate is a white, insoluble powder varying from $Bi(O_2CC_6H_5)_3.Bi(OH)_3$ to $Bi(O_2CC_6H_5)O$ in composition. It is prepared by the reaction of bismuth hydroxide and benzoic acid in water, and is used in medicine, largely as an antiseptic.

Bismuth subsalicylate or **basic bismuth salicylate** is a white powder of approximately the composition $Bi(O_2CC_6H_4OH)_3$, Bi_2O_3. It is insoluble in water but decomposed by acids and alkalies and is prepared by the reaction of bismuth hydroxide with salicylic acid. A U.S.P. grade which yields 62-66 per cent of bismuth trioxide is sold for use in medicine.

Bismuth subgallate or **basic bismuth gallate** is a bright yellow powder approximating $C_6H_2(OH)_3CO_2Bi(OH)_2$ in composition. This is insoluble in water but decomposed by acids or alkalies. It is prepared by the interaction in aqueous solution of bismuth nitrate, glacial acetic acid, and gallic acid, and is used in medicinal products. The U.S.P. grade yields on ignition 52-57 per cent of bismuth trioxide.

Bismuth sulfocarbolate, bismuth phenolsulfonate or **bismuth sulfophenylate,** $Bi(SO_3C_6H_4OH)_3$, is a reddish-white powder soluble in water or acids. It is obtained by the reaction of bismuth hydroxide and phenolsulfonic acid, for use in medicine.

Bismuth *beta*-naphthol or **bismuth *beta*-naphtholate,** $Bi_2O_2(OH),C_{10}H_7O$, is a brown to gray powder, almost insoluble in water or other solvents. It is prepared by treating a solution of sodium *beta*-naphtholate with an acetic acid solution of bismuth nitrate, and adding caustic soda solution to neutralize excess acid. It is used in medicine.

CHAPTER XIV

LEAD, SILVER, GOLD AND MERCURY

Lead, Pb, is a dull gray, soft metal industrially important both as the element and in the form of its compounds. As is usual this means that its price is relatively low. The metal dissolves in nitric and acetic acids. It dissolves in hydrochloric acid and in some concentrations of sulfuric acid under suitable conditions. The principal ore is the sulfide. Reduction methods are complex. The ore may be roasted to the oxide or sulfate and then heated with more sulfide to give the metal and sulfur dioxide. The oxide may be formed and reduced with carbon. The sulfide may be reduced with metallic iron or the equivalent, iron oxide and carbon. Commercially, combinations of these steps are used.

Numerous alloys are important such as Babbitt metal, solder and type metal, whose compositions are given under tin. Because of its resistance to acids and alkalies the metal is used to line chemical equipment. **Hard lead** is an alloy containing 10-15 per cent of antimony. An alloy with tellurium known as **tellurium lead** is an important alternative. Many small objects are cast of lead-tin compositions. Lead or lead alloy is used for items exposed to weather such as statuary, roofing, etc. The pure metal is limited in use by its softness, which is largely corrected by alloying. It is very heavy. Lead pipes for carrying water supplies have largely been superseded. Lead is a cumulative poison so that small amounts become dangerous if taken into the body over a long period of time. In powdered form lead catches fire readily. A paste of ground lead in oil is available. **Lead wool** is used as a packing material for pipe joints. Many lead compounds are used as pigments, which by definition means that they are available in very finely divided form.

Lead monoxide or **litharge,** PbO, is insoluble in water but soluble in alkalies, in lead acetate solution and in acids. It is yellow to orange and occurs naturally. Commercially it results from the atmospheric oxidation of molten lead. When the molten lead cools, an outside layer of lead oxide is formed which crumbles and flakes off readily. Small amounts of the next higher oxide, red lead, are usually present. The commercial powdered product is used for making lead salts, in the manufacture of glass, pottery and enamel, and in rubber compounding. A mixture with glycerine sets to a hard cement in a few hours, and is commonly referred to as **litharge cement.** It is prepared immediately before use.

Red lead, minium or **lead orthoplumbate,** having the formula Pb_3O_4, is not a true oxide, but a salt of the base $Pb(OH)_2$ and the theoretical acid, H_4PbO_4. Hence it is inert and has the structure $PbPbO_4$. It is bright red in color and insoluble in water and acids except acetic acid. Heating litharge in a current of air forms red lead. Some litharge is usually present in minium because of incomplete oxidation. Dry red lead is sold containing 95 per cent or less of Pb_3O_4, 97 per cent of Pb_3O_4 guaranteed, and 98 per cent of Pb_3O_4 guaranteed. It is used as a pigment, largely as a protective coating on structural steel. Since it is used in oil, a grade ground in linseed oil is sold. Its importance for this purpose is decreasing due to development of new forms of protective coatings such as those containing barium chromate. Miscellaneous applications include its use in storage battery compositions, match heads, etc.

Orange mineral has the same approximate composition as red lead but differs in color and in some properties. It is obtained by roasting white lead at a low red heat. Grades are American and French. It is used as a pigment, in protective coatings, oil cloth, etc.

Lead dioxide or **lead peroxide,** PbO_2, is brown, and insoluble in water and acids except acetic. It is produced by the nitric-acid oxidation of red lead. Lead dioxide is relatively expensive as compared to the other oxides and is used in storage batteries, as an oxidizing agent in synthetic organic chemistry, and for varied miscellaneous purposes.

Lead carbonate, $PbCO_3$, exists, but the commercially important form is **basic lead carbonate,** $Pb_3(OH)_2(CO_3)_2$, or

white lead. This very fine white pigment is insoluble in water but soluble in those acids which form soluble lead salts. It is one of the oldest pigments known, having been originally made from natural lead carbonate. The processes of manufacture depend on the action of moist carbon dioxide on finely divided lead, with acetic acid present as a catalyst. Thus it is fundamentally the reaction of carbonic acid on lead. It is also made by precipitation from solutions of lead salts with carbon dioxide. One form sold is as the dry product. Being produced as a wet material, drying can be obviated by mixing the wet white lead with linseed oil. The water is displaced by the oil and rises to the top over a paste of white lead in oil. This paste product is sold as **lead in oil.** White lead is widely used as a paint pigment, particularly in outside paints. It has the desirable characteristic of long life when applied in a good oil vehicle, and when it fails it does so by chalking, thus tending to maintain a good appearance. Other uses as a pigment are minor. The objection to white lead is mainly to its poisonous nature, because the compound dissolves readily in many acids. **Flake white** is an especially good grade in flakes, used by artists.

Lead sulfate, $PbSO_4$, is unimportant, but as with the carbonate, **basic lead sulfate,** $PbSO_4.PbO$, is an important white pigment. From the color it must be a true basic compound rather than a mixture, since lead oxide is colored. It is extremely fine and only slightly soluble in hot water or acids. One source is the controlled oxidation and sublimation of galena, which is mainly lead sulfide, at a high temperature. Zinc oxide is usually present in the product and the formula is only an approximate one. Roughly the commercial composition is 75 per cent of lead sulfate, 20 of lead oxide and 5 of zinc oxide. It is sold both dry and ground in oil for use in paints, in ceramics, and as a pigment in general. Lead sulfate is more resistant to sulfide fumes than white lead, which is stained fairly readily. It blends well with other pigments.

Sublimed blue lead is another basic sulfate of lead produced by sublimation of galena. The color is probably that of unconverted lead sulfide. It is blue-gray in color, resistant to corrosion, and insoluble in water or acids. It is often used in priming coats and for other pigment purposes.

Lead titanate, $PbTiO_3$, is an insoluble, pale yellow compound of lead oxide and titanium dioxide prepared by reaction of the oxides at an elevated temperature. Some lead sulfate and lead oxide are present as impurities. It is used as a paint pigment having an opacity about 60 per cent of that of titanium dioxide. While not usable in white paints, all tints except blue-gray can be obtained.

Lead chloride, $PbCl_2$, is white, slightly soluble in cold water but moderately soluble in hot. When crystallized from water it forms flaky crystals which, if shaken, give a characteristic "silver rain" effect. It occurs naturally and is also obtained by adding hydrochloric acid to a solution of a soluble lead salt. The commercial grade is sold as "pure." It is used in the preparation of other lead salts and of pigments.

Lead iodide, PbI_2, is golden yellow. Its solubilities are similar to those of the chloride, forming "golden rain" in cold water. It dissolves in potassium iodide or sodium acetate solutions. Lead iodide is prepared by the reaction of lead salts with potassium iodide and is used in bronzing, printing and photography.

Lead nitrate, $Pb(NO_3)_2$, is a white salt, very soluble in cold water and extremely soluble in hot. It is also soluble in alcohol. The nitrate is obtained by the action of dilute nitric acid on lead or lead oxide. It is used as a mordant in the textile industry, for the preparation of other lead salts, and in the manufacture of inflammable or explosive compositions. It is one of the most common soluble lead salts.

Lead chromate or chrome yellow, $PbCrO_4$, is a yellow pigment, insoluble in water but soluble in alkalies or mineral acids. It is formed by the reaction of lead acetate or lead chloride with a soluble bichromate. Dark, medium and light shades of the yellow compound are sold for use as a paint pigment, usually as C.P., meaning that extender has not been added.

Basic lead chromate, chromate red or **Persian red,** $PbCrO_4$, PbO, is obtained by boiling lead chromate with alkaline solutions. It is a bright red of good covering power, used as a pigment in paints and other mixtures. **Chrome orange or orange lead chromate** is similar but the conversion to the basic chromate is less complete; essentially therefore it is an intimate mixture of lead chromate and basic lead chromate.

Molybdate orange is an inorganic pigment also sold as **Ming orange,** approximating the composition $PbMoO_4,PbO,H_2O$, being similar to chrome orange except that chromium is replaced by molybdenum. It is more expensive than chrome orange but possesses greater color strength, so that only about a third as much is needed. It is used as a pigment in various products such as paint.

Chrome green is a mixture of chrome yellow and Prussian blue. The optical effect of mixing these colors to give green permits dark or bluish shades, medium, and light or yellowish shades. The chemical properties are those of the two pigments. The product is sold as C.P., meaning free from extender, at varying prices which increase with an increasing blue content up to 50 per cent. **Reduced chrome green** is the extended C.P. pigment with prices varying with a variation in color content at 5 per cent intervals. The use as a pigment is only limited by conditions under which one or the other color present in the mixture will fade, usually the blue, resulting in alteration of shade in use. Chrome green should not be confused with chromium oxide which is also green and is used as a pigment. **Tungstated brilliant green** and **tungstated emerald green** are shades of chrome green on which tungstic acid has been precipitated to make them more stable and fast to light. They are expensive.

Lead arsenate, $Pb_3(AsO_4)_2$, is a white powder, very slightly soluble in water. It is formed by the reaction of lead chloride with sodium arsenate, for use as an agricultural insecticide. Its relative insolubility in rain water and the poisonous nature of both the lead and arsenate radicals make it particularly effective and prolong the period of protection of plant life on which it is sprayed.

Tetraethyl lead or lead tetraethyl, $Pb(C_2H_5)_4$, while not an article of commerce as such because of patent restrictions, is an important synthetic product of the organic chemical industry. It is a high-boiling liquid miscible with alcohol, ether, gasoline, etc., but not with water. It is shipped in concentrated solution in solvents and added to gasoline as an anti-knock agent, permitting operation of motors at a higher compression.

Lead acetate or **sugar of lead,** $Pb(O_2CCH_3)_2,3H_2O$, is a white to brown salt, very soluble in water and slightly soluble in alcohol. It is a common soluble salt of lead and is made by the reaction of acetic acid with litharge, lead monoxide. Carbonate is apt to be present as an impurity, since carbon dioxide is absorbed from the air. The relatively unimportant off-color grades are usually from low-grade acetic acid. Broken brown, and broken, crystalline, granular and powdered white grades are sold. The U.S.P. grade contains 85.31-89.57 per cent of the anhydrous salt. It is used in medicine, as a mordant, for the weighting of silk, and in manufacture of other organic lead salts. **Basic lead acetate** exists of varied compositions such as $3Pb(OH)_4(O_2CCH_3)_2$. It is less soluble in water than the normal acetate and is used for many of the same purposes.

Lead stearate, $Pb[O_2C(CH_2)_{16}CH_3]_2$, is an insoluble lead soap obtained as a white to yellow paste when lead acetate solution is heated with a solution of sodium stearate. It is soluble in many organic solvents and is used as a drier in protective coatings and printing inks.

Lead oleate, $Pb[O_2C(CH_2)_7CH:CH(CH_2)_7CH_3]_2$, is a white lead soap prepared by the reaction of a solution of lead nitrate or acetate and sodium oleate. It is similar in properties and uses to the stearate and is also a rubber accelerator.

Lead linoleate, $Pb[O_2C(CH_2)_7CH:CHCH_2CH:CH(CH_2)_4CH_3]_2$, is another lead soap formed when a solution of lead nitrate or acetate is heated with a solution of sodium linoleate. The product is light in color and has solubilities and uses similar to those of the stearate. It is one of the most important lead driers.

Lead resinate, $Pb(O_2CC_{19}H_{29})_2$, is another lead soap prepared by heating a solution of lead nitrate or acetate with sodium abietate solution. Solubilities are similar to those of other lead soaps. Precipitated and fused grades are sold for use as driers in protective coatings and as a waterproofing agent.

Silver, Ag, is a white, shining metal, soluble in nitric acid and in strong hot sulfuric acid. It is relatively inactive and therefore some is found free. Much is recovered from ores with other mineral values. Some comes from copper ores. Nearly all lead ores contain silver, which is recovered by a process of "solvent extraction" with molten zinc. From silver ores, such as **argentite,** Ag_2S, **pyrargyrite,** Ag_3SbS_3, and **cerargyrite,** AgCl, varied processes may be used, but commonly extraction is with sodium cyanide solution. Reduction of compounds to the metal offers no great difficulty. Gold, when present, is usually recovered by electrolysis.

Silver has important uses in the arts as well as for coinage. It is used in leaf form for decorative purposes, sold in 3¾ x 3¾-inch books. Alloyed with 10 per cent of copper to harden it, it is **sterling silver.** Other alloys are also used in jewelry and tableware. Large amounts are used for silver plating of base metals. The properties desired are largely resistance to corrosion and decorative effects. Treated with sulfides it forms **oxidized silver.** The metal is often used directly for preparation of its salts, which are in general white and water soluble. It is essentially an expensive metal because of limited supply and international manipulations inherent in its use for coinage. Many of its important compounds, such as the chloride, bromide and iodide, which are used in photography, are produced in the process rather than purchased as such. Silver compounds are poisonous, and are covered by the Caustic Poison Act, given in Appendix A.

Silver nitrate or **lunar caustic,** $AgNO_3$, is a transparent crystalline salt extremely soluble in water, very soluble in alcohol and soluble in glycerine or ether. It is the most important compound of silver, and is obtained by treating free silver with dilute nitric acid. Silver nitrate decomposes in the presence of organic matter, particularly when exposed to light, forming the black oxide. The U.S.P. grade contains not less than 99.8 per cent of the pure nitrate. Silver nitrate is widely used where a silver salt is needed, as in photography, silver plating, in indelible ink, hair dye, for silvering mirrors, and in medicine.

Silver nucleinate or **nargol** is a dark brown to black silver proteinate, often hygroscopic, readily soluble in water. It is obtained by treating a salt of nucleic acid with a silver salt. The variable composition usually contains 20-25 per cent of silver. A U.S.P. product known as **mild protein silver** contains 19-25 per cent of silver. It is used in medicine as an antiseptic.

Amino silver proteinate, silver protein or **novargan** is another dark brown silver-protein complex. It is obtained by the reaction of amino acids or their salts with silver salts. This form contains about 7-9 per cent of silver and is used in medicine. A U.S.P. product known as **strong protein silver** contains 7.5-8.5 per cent of silver.

Gold, Au, because of its inactive chemical nature, occurs free in veins of quartz or mixed with alluvial sand. It is soluble in *aqua regia* to form the chloride. Small quantities are found in ores containing copper, lead, silver, etc. It also occurs as the mineral **sylvanite,** $(AuAg)Te_2$, in Colorado. Gold is separated from other metals by varied methods such as electrodeposition, and from gangue by amalgamation with mercury, or solution in sodium cyanide to form sodium aurocyanide. Recovery from mercury by distillation or from cyanide solutions by precipitation offers little difficulty. Gold forms no salts of great industrial importance. As a metal it is used in the form of gold leaf, for coinage, for dentistry, for gold plate and in other decorative ways. The leaf is quoted in books of various sizes. Pure gold is known as 24 carat, a designation of 14 carat means that the remaining 10 carats are of an alloying element. This is one use of the term **carat,** which is also a unit of weight equal to 200 mg. Copper is used in yellow gold alloys. **White gold** is a zinc alloy. An alloy is, strictly speaking, not called gold unless it is over 12 carat, therefore contains more than 50 per cent of gold. **Filled gold** means gold plated over another metal.

The production and use of gold are primarily matters of international exchange, as regulated by law based on custom. The price would in any case be high because of the relatively high cost of production and the comparative rarity of the element.

Auric chloride or **gold chloride,** $AuCl_3,HCl,3H_2O$, is a yellow to reddish salt, very deliquescent, light-sensitive, and very soluble in water. It is easily soluble in alcohol. Gold chloride is prepared by solution of gold in *aqua regia,* a mixture of 3 parts of hydrochloric acid and one part of nitric acid, followed by repeated evaporations to dryness with hydrochloric acid. Aside from this **yellow gold chloride** containing about 48 per cent of gold, an **acid, brown gold chloride** is sold as irregular brown masses containing 50-51 per cent of gold. It differs only in having some of the water of hydration removed. The uses are minor and are those of a soluble gold salt, as in medicine, photography, etc.

Gold-soda chloride is a mixture of gold chloride and sodium chloride, with the properties of the two salts. It is prepared by admixture or by neutralization of a hydrochloric acid solution of gold chloride of suitable concentration, with sodium hydroxide. Grades sold are U.S.P. IX and photographic. The former contains not less than 30 per cent gold, the latter not less than 20 per cent. Uses are in medicine and photography and for miscellaneous purposes as a dilute form of gold chloride.

Mercury or **quicksilver,** Hg, is the only liquid metal, and is soluble in nitric acid or in hot concentrated sulfuric acid. It has the bright shining appearance characteristic of metals. Mercury is obtained by decomposing mercuric sulfide by heat. The sulfide occurs naturally as **cinnabar,** HgS. A domestic product is sold. The metal has a low vapor tension, high specific gravity, and expands uniformly, which makes it a valuable material for use in barometers and thermometers. Mercury forms amalgams with the better known metals, except iron and platinum, and is used for the extraction of metals from ores, as well as in commercial amalgams. By definition an **amalgam** is an alloy with mercury. The metal is used to form mercury compounds, in mercury vapor lamps and as a catalyst. Its use as a heat-transfer vapor in boilers is limited by price and supply. Essentially it is expensive. Its compounds, if soluble in water, are poisonous and even the minimal vapor pressure of the metal can cause poisoning on long exposure. A U.S.P. grade of mercury contains not less than 99.5 per cent of the metal. It is used in medicine in varied forms, both as a metal and as compounds. It forms two series of compounds, monovalent and bivalent and both are important. Some of the mercuric compounds hydrolyze readily in water to basic salts unless excess acid is present.

Mercury and chalk or **gray powder** consists of a mixture of 38 per cent of mercury, 10 per cent of honey and 57 per cent of prepared chalk and is a U.S.P. product. It is insoluble in water, except for the honey, and is used in medicine.

Mercury mass or **blue mass** is a U.S.P. preparation of the composition 33 per cent mercury, 1 per cent mercury oleate, 10 per cent glycyrrhiza, 15 per cent althea, 9 per cent glycerine and 32 per cent honey. It is used medicinally.

Mercurial ointment contains a mixture of mercury, with wax, vaseline, etc. U.S.P. **strong mercurial ointment** contains 49-51 per cent of mercury, 2 per cent of oleate of mercury, 30 per cent of wool fat, 5 per cent of white wax, and 13 per cent of white petrolatum. It is used in medicine for external application. U.S.P. **mild mercurial ointment** or **blue ointment** contains 60 per cent of strong mercurial ointment corresponding to 29-31 per cent of mercury, 20 per cent of white wax and 38 per cent of white petrolatum.

Mercury oxide occurs in three forms, one mercurous and two mercuric compounds. **Mercurous oxide** or **mercury black oxide,** Hg_2O, is the water-insoluble compound formed by the action of caustic potash on calomel. It is unstable, forming mercury and mercuric oxide on exposure to light. When ammonium hydroxide reacts with mercuric nitrate, a mercurous oxide compound containing an NH_2 group is formed, approximately $Hg_2O,NH_2Hg_2NO_3$. This is sometimes called **black mercury oxide** or **ammoniated mercury nitrate.** Both are used in medicine.

Red mercuric oxide or **red precipitate,** HgO, is insoluble in water but soluble in acids. It is formed by decomposing mercurous nitrate by heat. N.F. and technical grades are sold for use as an oxidizing agent, as a pigment in anti-fouling paints, in medicine and for preparing other mercury compounds.

Mercuric oxide or **yellow mercury oxide,** HgO, is insoluble in water. It is precipitated on adding caustic soda or caustic potash to solutions of mercuric salts. The difference between the yellow oxide and red oxide is due to a difference in the state of subdivision. The yellow form is the more reactive. U.S.P. and technical domestic grades are sold. The U.S.P. grade contains not less than 99.5 per cent of mercuric oxide on a dry basis. It is used for much the same purposes as the red oxide but is preferred in medicine because of finer subdivision.

Mercuric sulfide, red mercury sulfide or **vermilion,** HgS, is very insoluble in water or acids. It is a bright scarlet powder obtained by heating mercury and sulfur together and collecting the sublimed mercuric sulfide. That sold is of English origin. The red pigment is used in medicine, but more especially for coloring expensive types of paint, rubber, sealing-wax, plastics, etc.

Mercuric diammonium chloride or **white precipitate,** $HgNH_2Cl,H_2O$, is soluble in water and to some extent in alcohol. It is prepared by precipitating mercuric chloride with an excess of ammonium hydroxide and is sold as a white powder or in lumps for use in medicine.

Mercury chloride occurs as two compounds. The term usually refers to calomel. **Mercurous chloride** or **calomel** is a very insoluble white substance. It occurs in nature and is also manufactured by subliming mercurous sulfate with common salt. The mercurous chloride condenses in the cool part of the chamber. The U.S.P. grade contains not less than 99.6 per cent of mercurous chloride on a dry basis. It is used in medicine, largely as a cathartic. **Mercuric chloride, mercury bichloride** or **corrosive sublimate,** $HgCl_2$, is moderately soluble in cold water, very soluble in hot, and very soluble in alcohol or ether. It is a white powder manufactured by subliming a mixture of mercuric sulfate with common salt. The U.S.P. grade contains not less than 99.5 per cent of mercuric chloride on a dry basis. It is sold in crystalline and granular forms and used in medicine, in the manufacture of other mercury compounds, in tanning, textile printing, lithography, photography, as a preservative of organic matter, and in metallurgy.

Mercury iodide is sold in two forms. **Mercuric iodide** or **red mercuric iodide,** HgI_2, is insoluble in water and slightly soluble in alcohol or ether. It dissolves in solutions of soluble iodides, and is obtained by the direct reaction of mercury and iodine, or by the reaction in solution of potassium iodide and mercuric chloride. The common red form undergoes a reversible change on heating, to a yellow form. It is used in medicine. **Mercurous iodide or yellow mercurous iodide,** Hg_2I_2, is a yellow powder which darkens on exposure to light. It is practically insoluble in all solvents except solutions containing an excess of soluble iodides, which convert mercurous iodide to the mercuric form. The mercurous salt is obtained by the reaction of potassium iodide with mercurous nitrate, and is used in medicine. The U.S.P. grade contains not less than 99 per cent of mercurous iodide on a dry basis.

Mercuric sulfate or **mercury bisulfate,** $HgSO_4$, is a white powder which is decomposed by water to a yellow **basic mercuric sulfate,** $HgSO_4,2HgO$. It is soluble in mineral acids or sodium chloride solution. The sulfate is prepared by the action of hot concentrated sulfuric acid on mercury. It is used in medicine, in the manufacture of corrosive sublimate, as a catalyst, and in the extraction of gold and silver from roasted ores.

Mercuric nitrate, $Hg(NO_3)_2$, is a white, deliquescent powder, easily soluble in dilute nitric acid but hydrolyzed by water to a basic salt. It is prepared by the solution of mercury in excess nitric acid, and is usually sold as a solution of rather indefinite composition containing excess acid. Its use is largely in the preparation of furs for felting into hats, the operation being known as **carroting.**

Mercuric nitrate ointment or **citrine ointment** contains mercuric nitrate and lard. It is made by adding 7 parts of nitric acid to 76 parts of warmed lard. This is then mixed with 7 parts of mercury dissolved in 10 parts of concentrated nitric acid. The ointment is used for external application both in the original concentration and diluted.

CHAPTER XV

MISCELLANEOUS METALS AND COMPOUNDS

These metals and compounds are grouped together here solely as a matter of convenience, and because of their lesser commercial importance—not necessarily because of any chemical relationship. This leads to an unavoidable contrast of metals, pigments, etc., of diverse origin and usage.

Platinum, Pt, is a silvery white metal with a gray tinge, which does not oxidize on heating. It melts at 1753° C., which renders it useful for heating to high temperatures, as in laboratory ware. Platinum is insoluble in all single acids but soluble in *aqua regia,* a mixture of 3 parts of hydrochloric acid and 1 part of nitric acid. It occurs free and also as **sperrylite,** $PtAs_2$. The high price prevents extensive use. From the solution in *aqua regia,* **chloroplatinic acid,** H_2PtCl_6,H_2O, is prepared, and from this in turn, the potassium salt, which is substantially insoluble. The oxide or the metal, distributed on suitable carriers such as asbestos or pumice, is a catalyst for many reactions, but has largely been replaced by less expensive materials. Other uses are mechanical, such as contact points for spark coils, etc., but there, too, platinum is being replaced because of its high price.

Tungsten, W, is a metal soluble in nitric acid, or in hot alkali hydroxide solution. It occurs in ores as the oxide, or as the tungstate of copper, lead or calcium. The principal mineral, **wolframite,** is essentially a manganese and iron tungstate, but **scheelite,** $CaWO_4$, is also important. Ores can be separated from a large proportion of impurities by gravity, owing to their high density, and from stannic oxide by magnetic methods. To separate tungsten, the crude concentrate is heated with excess soda ash to produce sodium tungstate, which is extracted with water. Tungstic acid is precipitated on acidifying, and this is changed to the oxide by heating. The acid and oxide can also be obtained by various other treatments.

Tungsten is prepared from the oxide by reduction with carbon if the metal is to be used in alloys, or reduction with hydrogen if the pure metal is needed in the form of a fine powder, as when it is to be used in electric light filaments. The powder is then compressed into rods which are sintered together by passage of an electric current. After further working this is drawn into wire. In commerce only the gray to black powder is normally quoted, of either 98 or 99 per cent purity. The metal is also an important alloying element in tungsten steels and is used as X-ray targets, for electrical contacts, etc.

Tungstic oxide, WO_3, can be obtained from wolframite as described in the preparation of the metal, or from scheelite by decomposing the finely ground ore with hydrochloric acid. The tungstic acid formed by the latter procedure is dissolved out of the sludge with ammonia. The complex ammonium compound can be converted to tungstic oxide by igniting. The oxide is used to form the metal by reduction, and for the preparation of tungstates. Being essentially acid rather than basic in nature, it is a true acid anhydride and is sometimes called **tungstic acid.**

Molybdenum, Mo, is a silvery white metal soluble in strong acids. It is obtained from a naturally occurring molybdenum sulfide ore, **molybdenite,** MoS_2, which is concentrated by gravity methods and roasted to the oxide. By extraction with ammonium hydroxide, ammonium molybdate is formed and separated. This gives a purified trioxide on ignition. The oxide is then reduced with carbon or hydrogen. The former leaves carbon in the metal. Reduction of the oxide with aluminum has also been practiced.

While the silvery metal can be separated, commercially it appears as a gray to black powder of 98 per cent purity. Its chief use is in molybdenum steel which in some applications replaces nickel, vanadium or tungsten steels. There are applications in the electrical industry but they are of minor importance.

Titanium dioxide, TiO_2, is a white pigment soluble in concentrated sulfuric acid or in alkali hydroxide solution. The latter solubility illustrates its acid-forming nature; it is also known as **titanic acid anhydride.** The impure dioxide occurs naturally as **rutile** and **anatase,** and combined in the form of **ilmenite,** $FeTiO_3$. The commercial supply is practically all obtained as ilmenite from Travancore, India. Titanates of other metals are also known. Titanium ranks tenth in abundance in the earth's crust. The natural dioxide is darkened by the presence of iron. It is converted to alkaline titanates and then titanic acid is precipitated with acid. This is ignited to the oxide, which is extremely finely divided. While its covering power as a pigment is high, the price is also high, so that aside from the sale of the pure pigment, it is also sold "let-down" with calcium sulfate, barium sulfate or magnesium carbonate. Titanium dioxide is also used as a source for the manufacture of other titanium salts, as a catalyst, and in special types of ceramics. Lead titanate is also an inorganic pigment.

Titanium potassium oxalate: See potassium titanium oxalate.

Vanadium oxide or **vanadium pentoxide:** See vanadic acid.

Zirconium oxide, ZrO_2, when pure is a white powder soluble in hot concentrated sulfuric acid and in hydrofluoric acid. It occurs in nature as **baddelayite.** This reacts on fusion with alkaline carbonates to form soluble zirconates and is therefore an acid oxide although not usually so designated. These zirconate solutions precipitate the hydroxide on acidification and this may be ignited to the oxide. The tetrafluoride obtained by reaction of the mineral with hydrofluoric acid also gives the dioxide on reaction with boric oxide. Both the crude ground product sold as 53 per cent and 73-75 per cent, and a white 98 per cent oxide are sold. Because of its refractory nature and high melting point the crude oxide is used in furnace linings, muffles and other refractory equipment and utensils. The purified grade is used in acid-proof enamel and in porcelain and opaque glass.

Zirconium nitrate, $Zr(NO_3)_4.5H_2O$, is obtained as a white crystalline product soluble in cold water and decomposed by hot. It is formed by the reaction of nitric acid and zirconium hydroxide, and is used as a preservative.

Uranium oxide or **yellow uranium oxide,** U_3O_8, is insoluble in water but soluble in strong acids. It occurs in crude form as **pitchblende** and is present in other uranium ores. Substances which may be present in such an ore are silica, thoria, rare earths, calcium, iron, lead, magnesium and other metallic compounds, as well as radium and helium from the radioactive disintegration of uranium. The ore is broken up and treated with a mixture of sulfuric and nitric acids. Uranium goes into solution and the insoluble sulfates of radium, lead, barium, calcium, etc., precipitate. Treatment of the filtrate with excess of sodium carbonate precipitates iron, aluminum and similar hydroxides, while uranium forms a double carbonate which remains in solution. The filtrate is next made alkaline with sodium hydroxide to precipitate the insoluble **sodium diuranate,** $Na_2U_2O_7,6H_2O$. On treating this with dilute acid the oxide is obtained. While it is an acid oxide, the salts are unimportant. Uranium oxide is used in making fluorescent glass, for coloring glazes for porcelain, in catalysts, and in the preparation of uranium salts.

Cerous hydroxide or **cerium hydrate** approximates the formula $Ce_2O_3,6H_2O$. It is insoluble in water but soluble in acids. The color varies with the purity, the pure hydroxide being white but being rendered yellow to brown or pink by the presence of other rare earths. The chief source is **monazite sand,** which contains a mixture of phosphates of the rare earths, the more important being cerium, lanthanum and thorium. Both the pure and crude cerium hydrates have a market but commonly the grade sold contains all of the rare earths from monazite sand except thorium. A major impurity is therefore **lanthanum hydrate.** Cerium hydrate is precipitated as a by-product in the thorium industry, from soluble salts of cerium. In a relatively pure form cerium hydrate is used to produce cerium salts and to impart a yellow color to glass. The crude material is used in the flaming arc lamp.

Cerium oxalate or **cerous oxalate,** $Ce_2(O_2CCH_3)_3,9H_2O$, is a white to pink salt insoluble in water or dilute acids but soluble in strong acids. It is obtained as a by-product in the production of thorium from monazite sand by precipitation from solutions of soluble cerium and lanthanum salts. Pure cerium oxalate can be obtained, but the U.S.P. IX grade quoted contains lanthanum, didymium, etc. Somewhat over 50 per cent of the material is cerium oxalate. It is used in medicine and as a relatively inexpensive source of mixed rare earths.

Thorium nitrate is a white, crystallized or solidified compound extremely soluble in water or alcohol. The formula of the commercial product is approximately $Th(NO_3)_4,9H_2O$. It is obtained by a lengthy purification process from monazite sand, cerium salts being separated as by-products. Freedom from other rare earths is essential and the price is relatively high. Thorium sulfate up to several per cent is commonly present. Thorium nitrate is used with a small amount of cerium nitrate in the manufacture of gas mantles, and as a source of pure thorium oxide.

Thallium sulfate, Th_2SO_4, is a white, crystalline compound resulting from the reaction of sulfuric acid on thallium oxide. It is moderately soluble in cold water, very soluble in hot. Thallium is more closely related to lead than to any other common element. Thallium sulfate is sold as a 99 per cent grade. Uses are largely in rat poisons and insecticides.

CHAPTER XVI

CARBON AND MISCELLANEOUS NONMETALS WITH THEIR OXIDES AND RELATED COMPOUNDS

As a matter of organization all compounds have been classified by their positive elements. This leaves the nonmetals and their oxides for separate consideration in this chapter. Similarly compounds composed of two nonmetallic elements fall into this classification.

Carbon, C, exists in a great variety of forms. All forms are insoluble in the ordinary reagents. **Diamonds** are pure carbon. In the clear, transparent form they are too expensive for abrasive use but off-color diamonds are an important abrasive for drilling and for cutting hard alloys.

Carbon black is a rather pure form of carbon in a very finely divided condition. It is obtained by burning natural gas with insufficient oxygen for complete combustion, and depositing the carbon on a metal surface in contact with the flame. This is also called **channel black** or **gas black** from the method of preparation. A standard grade and many special grades are usually quoted. Carbon black is the major black pigment used in printers' ink, rubber goods, varnish, paint, enamel, lacquer, and in numerous other products. The importance of carbon black in toughening and increasing the life of rubber goods can hardly be over-emphasized.

Acetylene black is more graphitic than carbon black, is produced by similar methods from acetylene, and is used for similar purposes. It is also used as a filler for oxygen type explosives and in dry cells, but use is limited due to high price.

Lampblack can best be compared with carbon black by describing the former as greasy, the latter as dry. It is obtained by burning by-products from the distillation of coal, petroleum, vegetable oils, tars, etc., with insufficient air for complete combustion. The process is similar to that for carbon black. Lampblack is a gray-black, rather than the deep black of carbon black. Grades are domestic and imported, of the same numbers as carbon black. Uses are similar to those of carbon black. It is much less expensive than carbon black for most grades.

Charcoal black is a soft black carbon obtained by the incomplete combustion of wood. It contains considerable inorganic ash. Grades are lump **hardwood charcoal, soft-wood charcoal,** powdered to pass 80-100 mesh, and powdered **willow charcoal.** It is used as a reactive grade for making calcium carbide, as a pigment in crayons and colors in oil, as an adsorbent in filtration, for adsorption of gases in gas masks, for decolorizing fats and oils, and for many similar purposes. Other grades of **activated carbon** or **decolorizing carbon,** made from special woods by careful control of temperature, are sold under trade names. The degree of activity of such activated carbons varies widely with different sources.

Vine black, or **Liege black** is obtained by the incomplete combustion of grape vine twigs and wine lees. It is relatively inexpensive. Grades A and B are sold for use in artists' colors and for general purposes.

Ivory black is a very intense black made by charring ivory cuttings and ivory dust. The genuine ivory black is expensive and used mainly as an artist's color in oil.

Graphite is a slippery, glistening, somewhat flaky form of carbon, and is both natural and manufactured. The natural mineral is mined and purified. The artificial material is produced from coal or charcoal by electric-furnace methods. The natural grade is higher in ash than the artificial. Grades sold are flake, 90 per cent through 325 mesh to contain 50 per cent of graphitic carbon; powdered, 90 per cent through 325 mesh to contain 65 per cent of graphitic carbon; and the same to contain 80 per cent of graphitic carbon. It is used as the "lead" in pencil manufacture, in arc-light carbons and electrodes, as a solid lubricant, in stove polish, in special paints, as a parting agent for foundry molds, and for varied miscellaneous purposes. It is sometimes known as **plumbago.** Unlike many carbons it is only combustible under extreme conditions.

Bone black or **animal charcoal** is a form of carbon high in ash, particularly in phosphates, and is obtained by calcining animal bones. Grades parallel those of carbon black. It is used as a pigment of lower covering power, and as a decolorizing agent in sugar refining. After use as a decolorizing agent, the usual practice is to reactivate by careful ignition.

Coal is an impure form of carbon resulting from decomposition of vegetable matter in past geological time, and hardly to be considered with the true carbons because of its high content of mineral matter and hydrocarbons. Its use as a source of carbon for heating and for the reduction of metal oxides and sulfides, in a sense classifies it as one of the commercial forms of carbon. **Coke,** produced by driving the volatile matter from coal, is also so used. For the reduction of the oxides of expensive metals, charcoal is occasionally preferred.

Carbon dioxide, CO_2, is a colorless, odorless gas, moderately soluble in water and alcohol. It is produced by combustion of carbon with an excess of oxygen, and also liberated by the action of acid on limestone. Commercially it is recovered from the gases from alcoholic fermentation, produced by controlled combustion of coke, or recovered from flue gases. The major item of its cost is in purification. The U.S.P. grade is 99 per cent pure. The gas is compressed as a liquid in cylinders containing 20-25 pounds, usually the latter, for use in the manufacture of carbonated beverages, or is converted into solid carbon dioxide, which is used as a refrigerant under the name of **dry ice.** Incomplete combustion of carbon produces another oxide, **carbon monoxide,** CO, which is highly poisonous and a strong reducing agent. It is not an article of commerce but is produced in many reactions as an active agent, and is present as a major ingredient in **coal gas, water gas** or **producer gas.** Carbon monoxide is produced as water-gas on a large scale for immediate re-use in synthetic methanol manufacture.

Carbon bisulfide or **carbon disulfide,** CS_2, is a colorless to light yellow, highly refractive liquid. It is slightly soluble in water and mixes with many organic solvents in all proportions. Production is by direct union of sulfur vapors with glowing carbon in the electric furnace, followed by condensation. The presence of other sulfur compounds as impurities gives the commercial product a characteristic disagreeable odor. Carbon bisulfide is an important solvent, as it dissolves sulfur, rubber, iodine and phosphorus. It is also used as a fumigant and disinfectant, and in the manufacture of carbon tetrachloride.

Chlorine, Cl_2, is a greenish yellow gas at ordinary temperatures, or a liquid under pressure. It is only slightly soluble in water to give **chlorine water** but dissolves in alkaline solutions by reaction, to form alkali hypochlorites. It is produced by the electrolysis of concentrated aqueous solutions of sodium chloride, sodium hydroxide being obtained as a commercial product at the same time. The chlorine is liberated at the anode, drawn off, dried with sulfuric acid, and refrigerated or compressed to change the gas to a liquid for storage in steel cylinders. Because of the upsetting influence on the market of the simultaneous production of chlorine and caustic soda, a process for its displacement from sodium chloride by oxides of nitrogen, giving sodium nitrate as the other product, has been introduced. The use of chlorine is so widespread that tank-cars have been developed for its transportation. These are in effect large pressure cylinders, the size of a railroad tank-car. The liquid is usually converted to gas by release through suitable regulators. It is used in water purification, in organic synthesis, to liberate bromine, and for treatment of ores for metal recovery. Either as the gas or more commonly in solution with sodium hydroxide or soda ash, it is used as a bleach for paper, wood pulp, cotton fabrics, shellac, and many other products.

Bromine, Br_2, is a dark red fuming liquid at ordinary temperatures. It is moderately soluble in water, giving **bromine water,** and readily soluble in alkaline solutions, forming hypobromites. It is obtained from the mother liquors of the table-salt industry, particularly those of Michigan, since sodium and magnesium bromides are more soluble than the chlorides. In one process the bromine is liberated by a stream of chlorine vapor, after which the bromine vapor can be condensed. Another method is to electrolyze the liquor containing bromides.

Requirements for the tetraethyl-lead industry have become so great that direct recovery of bromides from sea water is important. This is treated with the required amount of the more active halogen, chlorine, and the bromine displaced by aeration. It is then recovered by reaction with ethylene to give **ethylene dibromide.** Thus the bromine is not obtained as such in this process. Impurities which are apt to be present in bromine are chlorine, hydrobromic acid and bromoform. It is purified by shaking with potassium or calcium bromide and redistilling. Commercial and purified grades are sold for use in the manufacture of bromides, in organic synthesis, as an oxidizing agent, and for manufacture of other compounds of bromine. Since it is expensive, the uses are restricted to those where chlorine will not serve the purpose.

Iodine, I_2, is a dark brown, crystalline material at room temperature. It vaporizes directly by sublimation on heating, or slowly at room temperature, to give a violet vapor. Iodine is only very slightly soluble in water, but dissolves readily in aqueous solutions of alkali iodides, or in alcohol and other organic solvents. The alcoholic solution is known as **tincture of iodine.** The sources of iodine are more than adequate to meet the demand but the price is high, partially because of artificial restriction. A major source of iodine is sodium iodate which is present in the mother liquor obtained in the purification of Chile saltpeter. This liquor is allowed to react with the calculated amount of sodium bisulfite, when free iodine is precipitated. Iodine is purified by sublimation, which frees it from bromine, chlorine, and other impurities. Another source is from seaweed by boiling with sodium carbonate solution, precipitating alginic acid with hydrochloric acid, neutralizing the filtrate and evaporating to dryness. The recovery of iodine from the residue is from the resulting sodium iodate.

Crude and resublimed iodine crystals are sold, as well as U.S.P. tincture and a mild tincture. The regular U.S.P. tincture contains 6.5-7.5 grams of iodine and 4.5-5.5 grams of potassium iodide in 100 cc. of alcoholic solution. The mild U.S.P. tincture contains 1.8-2.2 grams of iodine and 2.1-2.5 grams of sodium iodide per 100 cc. of alcoholic solution. The

U.S.P. compound solution contains 4.5-5.5 grams of iodine and 9.5-10.5 grams of potassium iodide in 100 cc. of aqueous solution. The tincture deteriorates somewhat with time, due to reaction. Proprietaries known as "**organic iodine**" are also marketed as solutions. These are supposed to have the antiseptic value of iodine without its objectionable irritant characteristics. Uses of iodine aside from medicinal are in organic synthesis and for the preparation of iodides.

Sulfur, S_8, is a lemon-yellow element solid at room temperature. It is insoluble in water but dissolves in carbon bisulfide, and in hot nitric acid by reaction. There are both rhombic and monoclinic crystalline forms melting at 112.8° C. and 119.2° C. respectively. On further heating the liquid turns dark red and becomes very viscous.

Sulfur occurs widely distributed in nature, both in the free and the combined state. Natural sulfur is always contaminated with clay, limestone, etc. A simple method of purification is to melt the sulfur and drain it from heavier impurities. Not all impurities are separated by this method. The recovery from natural deposits is largely by the **Frasch process.** Superheated water under pressure, and compressed air, are forced through pipes into the natural deposits to bring the molten sulfur to the surface. This is allowed to congeal in large open tanks and subsequently may be further processed. As recovered by this process the product is 98 per cent pure, and the major portion is not further purified. When distilled and allowed to condense as a solid, it is in finely divided form known as **flowers of sulfur.** When melted and cast in molds it gives **roll sulfur.** As a cast material it is also known as **brimstone.** Ground, it is known as **sulfur flour.** Some is recovered as a by-product from industry in precipitated form, and called **precipitated sulfur.** This is usually rather impure. A pure precipitated grade can also be prepared by chemical reaction of various compounds, for example sodium thiosulfate and acids. Various grades sold are crude, flowers, broken, refined, commercial flour, rubbermaker's flour, extra fine flour, superfine flour, heavy flour, light flour, virgin rock and roll. U.S.P. grades are precipitated, sublimed, and that washed with ammonia-water; all contain not less than 99.5 per cent of pure sulfur on a dry basis.

Sulfur has largely replaced pyrites as the raw material for the production of sulfuric acid. It is used in large amounts as the vulcanizing agent in rubber, and is an essential ingredient of gunpowder. Molten sulfur with fillers is used as a corrosion-resisting cement. Applications in paper manufacture, plastics, etc., are multitudinous. It is also used in medicine.

Sulfur dioxide, SO_2, is a colorless, pungent gas, very soluble in water, giving a solution of sulfurous acid, described under acids. It is obtained by roasting iron pyrites, FeS_2, by purifying the gas obtained in ore-smelting furnaces, or, more commonly, by burning sulfur in air. The colorless gas can be changed to a liquid by subjecting it to a pressure of 3 atmospheres or by cooling to low temperatures. Sulfur dioxide is sold graded as a commercial liquid and of a much more expensive quality for refrigeration, usually in 150-pound cylinders. It is used as a bleaching agent for many types of products including straw, silk, sponges, oils and flour, as a preservative for meat, in the paper industry, as a disinfectant and fumigant, as a refrigerant, and as the major use in liquid form for purification of petroleum. It is made and re-used immediately in the manufacture of sulfuric acid.

Sulfur chloride or **sulfur monochloride,** S_2Cl_2, is an amber-colored to red fuming liquid which is decomposed by water but is soluble in the common organic solvents. It is produced as a by-product in the manufacture of carbon tetrachloride from carbon bisulfide and chlorine. Sulfur chloride is also obtained by passing chlorine over molten sulfur. It is used as a sulfur solvent in vulcanizing of rubber, for hardening woods, as an insecticide, in synthetic organic chemistry, and in the extraction of gold from its ores.

Sulfuryl chloride or **sulfur oxychloride,** SO_2Cl_2, is a low-boiling, colorless liquid with a characteristic odor, produced by the direct union of sulfur dioxide and chlorine. It is decomposed on contact with water but is soluble in glacial acetic acid. The major use is in organic synthesis.

Sulfur iodide or **sulfur subiodide** is obtained by fusing sulfur with iodine in the absence of oxygen. It is not the compound, sulfur monoiodide, and may be only a mixture of the two elements. It is gray to black in color and has an odor of iodine. The material is practically insoluble in water but dissolves easily in carbon bisulfide. A solution of potassium iodide extracts the iodine but alcohol does not. It is used for medicinal purposes, largely external.

Phosphorus, P_4, is obtained in two forms. **White phosphorus** is insoluble in water, moderately soluble in benzol, slightly soluble in alcohol or ether, soluble in alkalies, and very soluble in carbon bisulfide. It is the normal form commonly prepared from the natural calcium phosphate of degreased bones, or from phosphate rock. In manufacture, calcium phosphate is mixed with carbon and sand and fed into an electric furnace heated by an alternating current. At the very high temperature produced, the calcium silicate formed fuses to a liquid slag which can be withdrawn as such. The phosphorus oxide is reduced by the carbon to free phosphorus, which passes off as a vapor, mixed with carbon monoxide, into a condenser. The phosphorus is purified and cast into sticks in water-cooled forms. While the pure form of this type of phosphorus is white, the commercial form is **yellow phosphorus,** which contains a very small amount of red phosphorus formed by the action of light. Yellow phosphorus is very poisonous and is used in rat poison and insecticides. It is also used in making other phosphorus compounds and phosphor-bronze. Practically speaking, phosphoric acid is made from it in one process, although the phosphorus is not isolated as such. Yellow phosphorus is highly inflammable and may ignite spontaneously. It is therefore stored under water.

Red phosphorus is an allotropic form, theoretically unstable but practically very stable. It is insoluble in water and the solvents which dissolve yellow phosphorus. It is formed by heating white phosphorus to about 240° C. in the absence of oxygen. The product is freed from white phosphorus, after grinding under water, by treatment with caustic soda solution. Red phosphorus is stable to air and light, is much less reactive chemically than white phosphorus, and is nonpoisonous. It is used in making matches, in which the use of yellow phosphorus is prevented by prohibitive taxation. Since it is more expensive than the yellow grade it is used only where the other will not serve.

Phosphorus sesquisulfide, P_4S_3, is formed by heating phosphorus and sulfur together at a relatively low temperature. It is a yellow crystalline inflammable material, insoluble in cold water, decomposed by hot, and soluble in carbon bisulfide. Use is in the manufacture of matches to replace phosphorus and in synthetic organic chemistry. Other sulfides of similar but not identical properties are **phosphorus trisulfide** P_4S_6, and **phosphorus pentasulfide,** P_2S_5, used in the manufacture of synthetic organic compounds.

Phosphorus trichloride, PCl_3, is a clear, colorless, fuming liquid decomposed by water but soluble in most organic solvents. It is obtained by passing a stream of chlorine gas over melted phosphorus, over heated red phosphorus, or through a carbon bisulfide solution of yellow phosphorus. The liquid trichloride is obtained by fractional distillation. Phosphorus pentachloride may be present as an impurity but this can be removed by distilling with excess phosphorus. Phosphorus trichloride is used as a chlorinating agent in the manufacture of synthetic organic chemicals. By further treatment with chlorine, **phosphorus pentachloride,** PCl_5, is produced as a yellow fuming solid. Uses are parallel to those of the trichloride where a more strongly reactive agent is required.

Phosphorus oxychloride or **phosphoryl chloride,** $POCl_3$, is a clear, colorless fuming liquid prepared by the reaction of phosphorus pentachloride or hydrogen chloride with phosphorus pentoxide. The liquid decomposes in the presence of water and most solvents to form hydrochloric and phosphoric acids. It is used as a chlorinating agent in the synthetic organic chemical industry.

Silica is chemically a name for **silicon dioxide,** SiO_2. All forms of silica are insoluble in acids except hydrofluoric acid; with this they react to form gaseous silicon tetrafluoride, SiF_4. Silica is widely distributed, both free and combined as silicates.

All forms of silica are used to some extent as fillers in many products, varying in use according to the fineness of the grade. **Quartz crystals** are a fairly pure form of silica. **Sand** is a fine-grained form of silica. **Glassmakers' sand** is a grade practically free from iron, white in color and used in making up glass batches. Off-color grades of sand are used as building material and for sand blasting. The important property is that they be physically sharp particles rather than rounded, as is the case with **sea sand. Ground sand** or **quartz sand** is sold of many different particle sizes, such as 140 mesh, for use as a filler and as a finer abrasive than the natural sand. **Amorphous silica** is a term applied to a material produced by the natural leaching of silicates by water through many ages. It normally contains from 1 to 5 per cent of iron and alumina as contaminants. This grade may be white to brown, depending on the iron content. For most uses the color is an important element in determining price, white grades being preferred. Dry-ground material is sold as 95-97 per cent through 325 mesh. Wet-ground grades are 95-97 per cent through 325 mesh, 96-98 per cent through 325 mesh, 99 per cent through 325 mesh and through 400 mesh. The uses are as an abrasive, as an extender in paint, and for a multitude of other applications. When used in paint it is sometimes called **silex** or **painters' silex.**

Diatomaceous earth, infusorial earth, fossil flour or **kieselguhr** is a form of silica. The varied names are assigned different meanings in terms of quality, at times, but these are not standardized to a degree justifying quotation. Diatomaceous earth occurs as a soft, white to brown mineral resembling chalk in appearance, consisting of the siliceous skeletons of microscopic algae. Deposits are found in various parts of the world. When ground, and often calcined to remove organic matter and improve color, the material is very light, soft and adsorbent. Domestic and foreign grades are sold, usually under trade names, but vary in properties according to the shape of the diatoms of the deposit from which they are derived. Uses are varied, such as for clarifying sugar solutions, fruit juices, and all types of chemical solutions, promoting the fluidity of concrete, as a filler in plastics, tile, etc., and as an abrasive in silver polishes and dentifrices. Its softness and lack of scratching recommends it for the latter purposes when properly graded.

Rottenstone is the residue of siliceous limestone from which the calcareous matter has been washed away by natural waters. It consists largely of silica, usually 80-85 per cent, and 5-15 per cent of aluminum oxide, lime, iron and carbonates. The color is green to brown. Domestic and imported grades are sold, the latter in lump and powdered form. It is used as an abrasive, as in polishing and scouring materials, and as a filler in products like rubber.

Tripoli consists of friable silica derived from the natural leaching of rock. It is usually white, yellow or pink in color. Grades sold are air-floated, double-ground and single-ground. Tripoli is used as an abrasive in polishes, buffing compositions and scouring powders.

Pumice stone, pumice or **pumicite** is of volcanic origin and varies in composition according to the locality. It consists largely of silicates of aluminum and alkali metals. Calcium, magnesium, iron and titanium may also be present. The material reaches the surface of the earth in a molten condition, then hardens to a very light, glassy, porous rock. The color may be white, gray, yellow or brown. Superior grades of pumice will contain 65-75 per cent of silica, 12-15 per cent of alumina, and about 5 per cent each of sodium and potassium oxides. Its hardness on Moh's scale is about 6. Grades sold are American-ground, 60, 70, 90, 100, 110, 130, 140, 165, 185 and 200 mesh; and Italian. Another classification is by numbers and letters. Italian-ground pumice is much less expensive than a comparable grade when American-ground. It is used as an abrasive, as in polishes and buffing agents, and as a base for catalysts.

Water, H_2O, while not purchased as a chemical is important industrially, particularly as a solvent. It is mentioned to stress its relation to the subject. Available from supplies in every city, town and hamlet, it is of highly variable composition. Some supplies may contain only 40 parts per million of solids, others may exceed 500 parts. In some areas water is very hard, in others it is soft, meaning the presence of, or freedom from, calcium and magnesium carbonates and sulfates. While it may be softened by precipitation of the hardness with soda ash and/or trisodium phosphate this merely substitutes one salt for another. The calcium or magnesium salts are replaced by alkali carbonates or bicarbonates. Softening by passing the water through **zeolite**, a natural or synthetic hydrous aluminum silicate, accomplishes the same thing.

For many chemical purposes distilled water is essential. The quantitative factor or volume used, must be considered. Generally the quantity of water is great as compared with other materials, so that a small amount of impurity may become an important factor. Another way of expressing 500 p.p.m. of hardness is as 0.05 per cent of dissolved material.

One classification of water in terms of hardness is in grains per gallon rather than parts per million. The U.S.P. grain per gallon is 17.1 parts per million of calcium carbonate, or an equivalent amount of other calcium or magnesium salt. In general a **soft water** contains up to 5 grains of hardness, a **moderately hard water** 15-20 grains, and a **very hard water** 30 grains or more. Seawater contains 200 grains of hardness per gallon. In the use of these two standards, hardness and total solids in parts per million, one must bear in mind that dissolved solids are not necessarily hardness. When softened the water may contain more dissolved salts than before softening. Water is not only widely used as a solvent but is a reagent in many processes. In the electrolysis of sodium chloride solution, water is a reagent, in effect reacting with the sodium liberated to produce caustic soda and hydrogen. Likewise in the water-gas industry, water in the form of steam is an agent reacting with red-hot carbon to produce hydrogen and carbon monoxide.

Hydrogen peroxide, H_2O_2, is an oily liquid which enters commerce only in aqueous solution. It is prepared by the action of dilute sulfuric acid on barium peroxide, or by bubbling carbon dioxide through an ice-cold aqueous solution of barium peroxide. Another source is by distillation from acidified potassium or ammonium persulfate solution. Hydrogen peroxide readily decomposes on warming, forming free oxygen and water. It is an active oxidizing agent provided decomposition is prevented. In the bottled product, this is usually accomplished by addition of a stabilizer such as a salicylate. Industrially sodium silicate serves this purpose, if added at the time of use. Grading is usually by the volume of oxygen it will liberate per unit volume of solution. The U.S.P. grade offered is 10 volume and contains 2.5-3.5 grams of hydrogen peroxide per 100 cc. of solution. This is usually designated 3 per cent. For industrial use 30 per cent or 100 volume is offered. The 100 volume grade is sometimes called **perhydrol.** Use of hydrogen peroxide has increased to a point where aluminum tank cars are used for shipment. Hydrogen peroxide is used as a bleaching agent on cotton textiles, in the refining of oils, for the preparation of gelatin and other food products, for bleaching straw, bones, etc., as an oxidizing agent in photography and other processes, as an antiseptic agent as in mouthwashes, for the preservation of tanning extracts, in brewing, and as a catalytic agent in hydrolyzing starch. Use as an antiseptic in medicine is declining because of its destructive action on live tissue.

Hydrogen, H_2, is a colorless gas produced electrolytically incidental to the manufacture of chlorine and caustic soda, or by electrolysis of water to give hydrogen and oxygen. It is sold in cylinders under pressure. The major application is at the point of production in the manufacture of synthetic ammonia, synthetic methanol, or to react with chlorine to produce hydrochloric acid.

Oxygen, O_2, is a colorless gas recovered from liquid air, and sold in pressure cylinders as an aid in welding, for medical use and miscellaneous purposes. Oxygen from the air is often a necessary chemical entering into the reaction; in other cases its presence may be undesirable. Its reaction is sometimes prevented by displacing the air with an inert gas such as nitrogen, hydrogen, or carbon dioxide.

Nitrogen, N_2, is also a colorless gas recovered from liquid air and sold to a limited extent in pressure cylinders. The major amount is consumed in synthetic ammonia manufacture.

For that purpose it is often obtained by burning the oxygen out of the air and absorbing the carbon dioxide.

Helium, He, is a rare gas found as a trace in the atmosphere but commercially largely recovered from natural gas from oil wells in the southwestern United States. It is sold in 200-cubic-foot cylinders but is very expensive. Its use in rigid or semirigid dirigibles as a gas for inflation, is possible only because of large-scale production under government control, a supply not commercially available. It is also used for filling electric bulbs. Other rare gases available at high prices are **argon, neon, krypton** and **xenon.** Of these argon is used in electric bulbs to some extent, neon is used in the familiar reddish neon lights, and the last two find lesser use in electric bulbs, particularly on continuous service.

CHAPTER XVII

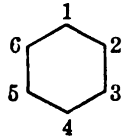
HYDROCARBONS, OTHER THAN THOSE FROM PETROLEUM, AND THEIR SIMPLE HALOGEN DERIVATIVES

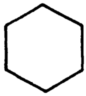
Fundamentally most of our more complex compounds are produced from the **hydrocarbons,** simple compounds of carbon and hydrogen such as ethylene, benzene, naphthalene, etc. Complex types of compounds from natural sources are often alcohols or esters, exceptions that do not alter the rule. Therefore the hydrocarbons are introduced as the first class of organic materials. Those from petroleum form a separate chapter. The halogen derivatives which are easily derived from the hydrocarbons are so closely related that they are included in this chapter. However, those halogen derivatives which are closely related to and derived from more complex types of compounds, are classified with those compounds.

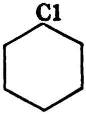
Some preliminary explanation of organic nomenclature is desirable. Organic chemistry is divided into **aliphatic compounds** or **straight-chain compounds** and **aromatic compounds** or **cyclic compounds.** The straight-chain hydrocarbons are often called **paraffins** regardless of molecular size, and the cyclic type **coal-tar derivatives** regardless of whether that was their source.

The position of substituted groups in an organic compound is usually shown by the use of numbers or Greek letters. The latter may be printed as such in italics, or may be spelled out. In an open-chain formula the carbon atoms are numbered, starting with the last carbon atom as one. Thus, $CH_3CH_2CH_2CH_2OH$ is 1-butanol and $CH_3CH_2CH(OH)CH_3$ is 2-butanol, the number showing the position of the substituted group, in this case the hydroxyl radical. Halogen and other radicals would be indicated in the same way, as 2-bromobutane, $CH_3CH_2CHBrCH_3$. Straight-chain acids show the position of a substituted group by calling the carbon atom adjacent to the carboxyl or COOH group the *alpha*-carbon atom, the one second from the carboxyl group the *beta*-carbon atom, the third *gamma*, etc. Thus $CH_3CHBrCOOH$ is *alpha*-bromopropionic acid and CH_2BrCH_2COOH is *beta*-bromopropionic acid.

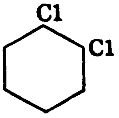
The simplest cyclic compound, benzene, is represented structurally by a hexagon with a carbon atom at each point, and is numbered clockwise, starting with number one at the top. It is understood that a hydrogen atom is attached to each carbon atom. When two radicals or side-chains are substituted in place of the hydrogen in adjacent or the 1,2 positions, the resulting compound is called an *ortho*-compound. When the groups are in the 1,3 positions the compound is called a *meta*-compound; in the 1,4 positions a *para*-compound. These are sometimes expressed by italicized letters, *o*, *m* and *p*. When three groups are substituted in the ring, numbers are used to indicate their position. As a convenient chemical shorthand these are often represented as indicated by the examples below.



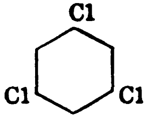

Benzene
C_6H_6



Chlorobenzene
C_6H_5Cl

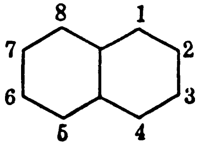


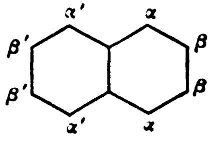
Ortho-di-chlorobenzene
$C_6H_4Cl_2$



1,3,5 Tri-chlorobenzene
$C_6H_3Cl_3$

Naphthalene is represented as two benzene rings sharing two adjacent carbon atoms. The one position is at the top of the right ring and the numbering is clockwise, omitting the two shared carbon atoms in the middle, giving 8 numbered positions. The 1,4 positions are also called *alpha*, the 2,3 positions *beta*, the 5,8 positions *alpha'* and the 6,7 positions *beta'*. The structural representation is as follows:





Thus *alpha*-naphthol has the hydroxyl, OH, group in the 1 or *alpha* position adjacent to a shared carbon atom. *Beta*-naphthol has the hydroxyl group in the 2 or *beta* position. There are two positions for *alpha* or *beta* because the structure is the same whether you consider the formula in a given position or inverted.

Mono compounds are not usually so designated, as it is assumed that only one radical is substituted in the compound unless otherwise indicated. **Di** compounds are those having a radical substituted twice, **tri** compounds three times, up to **hexa** compounds which have a radical substituted 6 times. Thus dichlorobenzene is $C_6H_4Cl_2$ and hexachlorobenzene is C_6Cl_6. In lists where compounds are arranged alphabetically these prefixes are considered part of the name, while numbers and Greek letters are not. When *ortho, meta* and *para* are spelled out rather than indicated by *o, m* and *p* they are considered part of the name.

Structure is also shown by the modifying terms, normal, secondary and tertiary. A normal compound has no side-chains; each carbon atom is linked to two other carbon atoms, as in normal propyl alcohol, $CH_3CH_2CH_2OH$. A secondary compound has two carbon atoms linked to a third carbon atom, as in secondary propyl alcohol, more commonly expressed as isopropyl alcohol, $(CH_3)_2CHOH$. A tertiary compound has three carbon atoms linked to a fourth atom, as in tertiary butyl alcohol, $(CH_3)_3COH$.

Methyl chloride or chloromethane, CH_3Cl, boils at about −24° C. and is therefore a gas at ordinary temperatures and pressures. It has a pleasant odor, is slightly soluble in water and very soluble in alcohol or ether. Methyl chloride is made from methyl alcohol, sodium chloride and sulfuric acid by distillation. Because of its low boiling point and ready condensation under pressure it is used as a refrigerant. A grade suitable for that purpose is sold. It is also a reagent in organic synthesis. The next member of the series is **methylene chloride or dichloromethane,** CH_2Cl_2, which is commercially unimportant and relatively expensive.

Methyl iodide or iodomethane, CH_3I, is the simple derivative of methyl alcohol and hydriodic acid produced by distillation of methyl alcohol from iodine and red phosphorus. Although colorless when fresh, the liquid develops color due to liberation of iodine when exposed to light, and is therefore usually yellow to brown. It is soluble in ether or alcohol, and aside from medicinal properties, is an important reagent in organic synthesis. **Methyl bromide,** CH_3Br, is similarly used in organic synthesis but is a gas at ordinary temperatures.

Chloroform, $CHCl_3$, is a colorless liquid of a characteristic sweetish odor, slightly soluble in water and miscible with alcohol or ether. It is manufactured by the action of bleaching powder or sodium hypochlorite on acetone or ethyl alcohol. U.S.P. and technical grades are sold. The U.S.P. grade contains 0.5-1.0 per cent of alcohol. It is an important solvent, since it dissolves rubber, fats, alkaloids, etc. Chloroform is noninflammable but the vapors in contact with flame form an oxidation product, carbonyl chloride or phosgene, $COCl_2$, which is both irritating and poisonous. It is used as a spotting fluid by dry cleaners and as an anesthetic.

Bromoform, $CHBr_3$, resembles chloroform in general properties and solubilities. Because of the bromine content it is more expensive. It is obtained by heating acetone or alcohol with bromine and caustic soda solution, and distilling. The U.S.P. grade sold is from the IX edition and contains up to 4 per cent of alcohol. Uses are largely medical.

Iodoform, CHI_3, consists of lustrous scales or crystals, or a yellow powder, and is insoluble in water, slightly soluble in alcohol and moderately soluble in ether. It is a U.S.P. product prepared by the combined action of iodine and aqueous potassium hydroxide on ethyl alcohol, acetone, acetaldehyde or a similar organic compound, or by electrolyzing a solution of potassium iodide in the presence of acetone or alcohol. It is used as an antiseptic dressing and for other medical purposes.

Carbon tetrachloride, CCl_4, is manufactured by the reaction of chlorine with carbon bisulfide in the presence of antimony pentasulfide, which acts as a carrier. Carbon tetrachloride is a noninflammable organic liquid practically insoluble in water but miscible with alcohol or ether. Ordinary and fire-extinguisher grades are sold. It acts as a fire extinguisher because the heavy vapors displace the air and thus prevent combustion.

Carbon tetrachloride is an important fat and oil solvent and is much used as a household fabric cleaner. It is also used as the cleaner in some automatic dry-cleaning machines. A disadvantage in its commercial use is that it reacts slowly with water to form hydrochloric acid which in turn attacks metals. The fumes are moderately toxic. In the presence of a flame or of hot metal it is partially converted to phosgene, $COCl_2$, which is highly toxic.

Ethylene, C_2H_4, is a hydrocarbon gas important as a starting material for synthesis. It has a faint, pleasant odor, is unsaturated, and has the structure $H_2C:CH_2$. Ethylene is produced from ethyl alcohol by chemical removal of a molecule of water. Commercially, supplies are also obtained by passing acetylene and hydrogen over a nickel catalyst, from the cracking of petroleum oil, and from natural gas. The production from acetylene is the important source. It is not an article of commerce to any great extent, being used only in purified form from small pressure cylinders as an anesthetic, and for the artificial ripening of fruit. Generally producers use it for conversion to other products. Some is used as a fuel to give a hot flame for cutting and welding.

Ethyl chloride or **monochloroethane,** C_2H_5Cl, is a gas at ordinary temperatures and pressures, since it boils at 12.5°C. when pure. It is slightly soluble in water, very soluble in alcohol and mixes with ether. The vapor is highly inflammable. Ethyl chloride is made by distillation of a mixture of ethyl alcohol and phosphorus chlorides, or in the same way as methyl chloride. It is sold in drums under pressure and used as a solvent, as a refrigerant and in organic synthesis as a reagent. There is a U.S.P. grade, with a specific gravity of 0.921 at 0°C., and a boiling point of 12-13°C.

Ethyl bromide, C_2H_5Br, is a clear, colorless liquid, slightly soluble in water and miscible with alcohol or ether. It is prepared by mixing absolute ethyl alcohol with red phosphorus, adding bromine slowly and distilling, or by distilling alcohol and hydrobromic acid in the presence of sulfuric acid. Methyl bromide is used in medicine, in synthetic organic chemistry and to a limited extent as a fire extinguisher.

Ethyl iodide, C_2H_5I, is a clear, colorless, heavy liquid, slightly soluble in water and soluble in alcohol or ether. It is prepared by distilling ethyl alcohol with red phosphorus and iodine. Uses are in medicine, and as a reagent in synthetic organic chemistry.

Ethylene chloride, dichloroethylene or **ethylene dichloride,** CH_2ClCH_2Cl, is a colorless liquid, slightly soluble in water but soluble in alcohol and miscible with ether. It is prepared by the direct union of ethylene and chlorine. Ethylene dichloride is used as a relatively inexpensive synthetic solvent for oils, waxes, gums, etc. It is also used for synthetic purposes, and to a small extent medically. Unless blended with about one-third of its volume of carbon tetrachloride, it is inflammable. The noninflammable mixture is used as an insecticide in vapor form, and as a solvent.

Ethylene bromide or **ethylene dibromide,** CH_2BrCH_2Br, is a volatile liquid prepared by union of ethylene and bromine. Its solubilities are similar to those of the dichloride. It is expensive, so its uses are limited to organic synthesis and minor medical applications. It is required in large volume for the manufacture of tetraethyl lead.

Trichloroethylene, $CHCl{:}CCl_2$, is a colorless liquid prepared by boiling acetylene tetrachloride with milk of lime or by passing it over heated barium chloride. It is insoluble in water but miscible with alcohol or ether. Trichloroethylene is a very good noninflammable fat solvent and does not form hydrochloric acid on standing with water to the degree that carbon tetrachloride does. Its applications are as an organic solvent of the nature of carbon tetrachloride. It is somewhat more expensive than the tetrachloride.

Tetrachloroethylene, carbon bichloride, carbon dichloride or **perchloroethylene,** $CCl_2{:}CCl_2$, is a noninflammable colorless liquid prepared by treating pentachloroethane with caustic soda. It is insoluble in water but miscible with alcohol or ether. C.P. and technical grades are sold, the two differing widely in price. It is used as a solvent in various applications, as in dry-cleaning soaps and detergent products, and is also applied in organic synthesis.

Tetrachloroethane or **acetylene tetrachloride,** $CHCl_2CHCl_2$, is a noninflammable colorless liquid formed by the complete reaction of acetylene and chlorine. It is slightly soluble in water but miscible with alcohol or ether. This is more expensive than solvents of the type of carbon tetrachloride but not excessively so. It is used as a solvent for oils and fats, as an insecticide, and in the manufacture of photographic film, although it is somewhat more toxic than the other solvents of its class.

Propylene, $CH_3CH:CH_2$ and **butylene,** $CH_3CH_2CH:CH_2$, have natural sources and properties similar to those of ethylene, but are used almost entirely by the producers for organic synthesis.

Propylene dichloride, $CH_3CHClCH_2Cl$, may be visualized as the methyl derivative of ethylene dichloride, and has similar properties and uses.

Amylene, C_5H_{10}, has numerous possible isomers. The commercial product is a mixture of isomeric compounds in which $(CH_3)_2C:CHCH_3$ and $CH_3CH_2CH:CHCH_3$ predominate. It is miscible with alcohol or ether but insoluble in water. The product is prepared by the dehydration of fusel oil or ordinary amyl alcohol with zinc chloride, but is commercially isolated from casing-head gasoline. Amylene belongs to the ethylene series of unsaturated hydrocarbons. The colorless, volatile, inflammable liquid has a disagreeable odor. It is used in medicine as a local anesthetic, and in organic synthesis in large volumes because of its reactivity and relatively low price.

Amyl chloride, $C_5H_{11}Cl$, is a term which may apply to various structures. All are colorless to light yellow liquids, miscible with alcohol or ether. **Normal amyl chloride,** $CH_3(CH_2)_4Cl$ is prepared by distillation of amyl alcohol with salt and sulfuric acid, or synthetically by addition of hydrogen chloride to amylene. **Mixed amyl chlorides** may contain any of the various possible structures but usually only one halogen in the molecule. The normal and mixed compounds are used in organic synthesis. The mixed chlorides are relatively inexpensive and are used as solvents and soil fumigants.

Dichloropentane, $C_5H_{10}Cl_2$, is a mixture of isomeric compounds prepared by the chlorination of amylene. About 40 per cent consists of **amylene dichlorides,** which have the chlorine attached to adjacent carbon atoms. It is a colorless to light yellow liquid insoluble in water but miscible with alcohol or ether, and is used as a solvent and in organic synthesis.

Dipentene, diamylene or **inactive limonene,** $C_{10}H_{16}$, is the racemic form of the terpene, limonene, obtained from oil of elemi, oil of wormwood and some grades of turpentine. The commercial product is produced by polymerization of trimethylethylene. The colorless liquid is insoluble in water but miscible with alcohol or ether. It has a lemon-like odor when pure and is used in a technical grade as an inexpensive solvent of low volatility.

Benzene or **benzol,** C_6H_6, is the simplest of the cyclic or aromatic hydrocarbons and is obtained in the destructive distillation of coal by the refractionation of coal tar distillate, followed by purification. It is also recovered from illuminating gas by absorption in oil and fractional distillation. Benzene is a colorless, volatile and inflammable liquid of substantial toxicity, insoluble in water but miscible with alcohol or ether, and boiling at approximately 80°C. The impure product may contain toluene, xylene and traces of tarry substances.

The highest grade is **nitration benzene,** a highly purified hydrocarbon for chemical synthesis. **Industrial pure benzene** as known in the trade boils within a range of 2° C. and approaches the purity of the nitration grade. **Ninety per cent benzene** or **industrial 90 per cent benzene** distils over the range from 77° to 120°C. and is a mixture of hydrocarbons of coal-tar origin containing at least 90 per cent of benzene. The 50 per cent grade of benzene contains higher homologues as contaminants. The different grades are selected according to use, 90 per cent benzene being usually satisfactory for solvent purposes. **Motor benzol** is a grade of rectified crude, suitable only for blending unless further rectified. It has been substantially freed from carbon bisulfide by distillation and from thiophene by sulfuric acid treatment. It distils 75 per cent below 100°C., 90 per cent below 120°C. and completely below 125°C. Benzene is used as a solvent for fats, waxes, resins and rubber in various industries, and for the synthesis of innumerable organic compounds, since it is the basis for an entire class of aromatic compounds, comprising a major proportion of those prepared synthetically. From such simple derivatives as nitrobenzene, aniline, chlorobenzene, and azobenzene, other more complex compounds are made, which are used as dyes, drugs, etc. When available, substantial volumes of the cheaper grades are blended with gasoline. The supply has been steadily increasing over the past few decades due to the use of by-product coke ovens in place of beehive ovens. The latter do not recover the benzol and other by-products from coal distillation.

Coal tar is a viscous oily fraction obtained in the distillation of bituminous coal to produce gas and coke. It must however, be more closely defined than that. **Low-temperature distillation tar** is obtained below 650°C. and is free from aromatic hydrocarbons which are present in coal tar. By definition coal tar is distilled at 900-1200°C. Tar from vertical retorts differs from that from horizontal retorts and a distinction is often made between the two. Strictly interpreted, coal tar means that from horizontal retorts. Carbonaceous materials such as lignite are mixed with the coal in some countries and cause a variation in the quality of the tar.

Coal tar is to be considered a crude material, the entire semiliquid distillate from the coal, after separation of an aqueous ammoniacal solution. It is almost entirely aromatic in nature and is the source of several crude fractions from which are synthesized the so-called **coal-tar chemicals.** Over 100 individual substances have been isolated as present in coal tar, but the separation of many of these is not commercial.

As quoted, coal tar is classified as crude or refined coal-gas tar and crude or refined water-gas tar. The crude contains up to 4 per cent of entrained water. It is used to a limited extent as a waterproofing agent, roofing material, for tarring ropes, in road construction, in paints, etc. However, partially refined fractions rather than the crude are used for nearly all purposes. The crude is so complex as to be only partially soluble in most solvents. The major use is for distillation to further fractions.

A preliminary distillation yields approximately the following fractions: crude naphtha up to 110°C.; light oil to 200°C.; crude phenol, light creosote or middle oil to 250°C.; heavy creosote or creosote oil to 280°C., anthracene oil to 350°C. and coal-tar pitch as residue. These are varied according to market demand, such as by taking a cut from the distillate at 160-180° C. for cumarone and indene.

Prepared tar has been partially distilled, usually up to the creosote-oil fraction. This soft coal-tar pitch is often blended with creosote, asphalt, bitumen, etc. for road tar, roofing impregnation, and use as a protective coating.

Coal-tar pitch is the dark brown to black amorphous residue after coal tar is redistilled, and amounts to 50-60 per cent of the usual grades of coal tar. It is a solid, sold as softening at 160° F. It is used as a binder for coal briquets, as an ingredient in compounded protective coatings, as a binder in electrode manufacture, in electrical insulating compounds and in many miscellaneous ways where an inexpensive thermoplastic is required. **Wood-tar pitch** is similarly derived from wood tar and similarly used.

Crude naphtha contains mostly benzene and toluene and is first washed with 10 per cent aqueous sodium hydroxide to remove phenols, then with dilute sulfuric acid to remove basic materials. It may also be agitated with concentrated sulfuric acid to destroy olefinic compounds and other reactive substances. After washing with water to remove acid the material is fractionally distilled with greater or less care, according to the grade of benzene and toluene desired.

Light oil contains mainly higher homologues of benzene with some phenol and pyridine. The oil is treated in the same way as the crude naphtha to remove acidic and basic substances, and distilled to give various hydrocarbon fractions. **Pyridine** is isolated from the acid extracts of crude naphtha, light oil and other fractions. It is fractionally precipitated by ammonia, then liberated by caustic soda, and purified by distillation from the crude black oil in which it is first isolated.

Light creosote or **middle oil** contains phenol, cresols, naphthalene, etc. It is usually solid at ordinary temperatures. The crude naphthalene is separated by crystallization from the phenolic bodies and isolated by pressing. This is then purified by alkali washing, acid washing and distillation or sublimation. The crude phenolic liquid contains basic substances and residual hydrocarbons, with up to 35 per cent of phenols. It is processed as described for crude naphtha but gives much more of the crude sodium phenolate fraction. That from other fractions may be added. This is steam-distilled to remove dissolved hydrocarbons or carbon dioxide, and the crude phenol which separates is distilled, The fraction up to about 180°C. is **crude carbolic acid** or **crude phenol,** higher fractions **cresylic acid.** By further fractionation, phenol, various cresols, xylenols, etc. may be isolated. Naphthalene and pyridine are isolated from the acid- and alkali-insoluble, and the acid-soluble fractions, respectively.

Heavy creosote or **creosote oil** contains phenol, creosote, naphthalene, anthracene, etc. The naphthalene may be distilled over in the first fractions, leaving **tar-acid oil,** containing up to an equivalent of 30 per cent of phenol. The creosote oil may also be worked up further. **Crude quinoline** bases can be extracted with sulfuric acid. From these **isoquinoline** can be purified by fractional precipitation with ammonia. **Indole** is extracted with caustic potash from the neutral oils of the creosote-oil fraction, and liberated with water. **Acenaphthene** is distilled at 260-270°C. and purified by crystallization from alcohol.

Anthracene oil is semi-solid at room temperature but liquid at 60°C. By pressing out the oils it is purified to 30-40 per cent anthracene, along with methylanthracene, phenanthrene, acenaphthene, diphenyl, pyrene, carbazole, acridine, etc. Phenanthrene is present in substantial amounts and is extracted with naphtha. Carbazole, another major ingredient, is extracted with pyridine. Fluorene is isolated by treatment with solid caustic potash. The anthracene oil is also often left with the coal-tar pitch, the distillation being stopped after the creosote oil is separated.

Phenyl chloride, chlorobenzene or **monochlorobenzene,** C_6H_5Cl, is a colorless liquid insoluble in water but miscible with alcohol or ether. It is prepared by passing chlorine into benzene in the presence of molybdenum chloride. The action is stopped when the monochloro derivative is obtained, as shown by the increase in weight. It is used in organic synthesis for the preparation of numerous compounds including the sulfur-black series of dyes. Chlorobenzene is unimportant except for preparation of other benzene derivatives. The term chlorobenzene is sometimes confused with **benzyl chloride,** $C_6H_5CH_2Cl$ which is entirely different in reaction. The corresponding **phenyl bromide** or **bromobenzene,** C_6H_5Br, is occasionally used but is much more expensive than phenylchloride.

Diphenyl, $C_6H_5C_6H_5$, is a white to light yellow crystalline compound insoluble in water, moderately soluble in methyl or ethyl alcohol or ether. It is prepared by passing benzene through a red-hot tube, or in small quantities by the action of sodium on an ethereal solution of bromobenzene. Diphenyl is used in organic synthesis for the preparation of materials used as disinfectants, dyestuffs, etc. It is also a heat transfer medium at high temperatures.

Diphenylmethane or **benzyl benzene,** $(C_6H_5)_2CH_2$, is a colorless crystalline compound insoluble in water but very soluble in alcohol or ether. Its melting point is 27° C., slightly above room temperature. It is made by the condensation of benzyl chloride and benzene in the presence of aluminum chloride or zinc dust and heat, or by the reaction of benzene with formaldehyde. Use is in organic synthesis, in particular in making benzophenone and dyestuffs, and as an odorant, such as in soap, to replace geranium oil.

Chloroacetophenone, $C_6H_5COCH_2Cl$, is prepared by the reaction of benzene with chloroacetylchloride in the presence of aluminum chloride. The white to light brown crystalline product is slightly soluble in water but very soluble in alcohol or carbon bisulfide. It is used as an intermediate in organic synthesis, and as a tear gas is effective at one part to 3 million parts of air.

Dichlorobenzene, $C_6H_4Cl_2$, can exist as three isomers, *ortho*-**dichlorobenzene,** *meta*-**dichlorobenzene** and *para*-**dichlorobenzene.** Two are important commercially, the *ortho* and *para* compounds. A mixture of these containing a little of the *meta* compound, is prepared by the controlled chlorination of benzene or chlorobenzene, and separated by pressing. The *para* compound is a white crystalline material of characteristic odor, miscible with alcohol and very soluble in ether but insoluble in water. It is used in organic synthesis, as deodorant blocks, and in moth-proofing and insecticidal preparations. The *ortho* compound is a nearly colorless liquid, insoluble in water, very soluble in ether and miscible with alcohol. Because of its status as a by-product of the *para* isomer the price is much lower, demand being limited. It is used in organic synthesis, as a relatively nonvolatile solvent, as a fumigant, and for varied miscellaneous purposes. Some grades of mixed dichlorobenzenes containing **trichlorobenzene,** $C_6H_3Cl_3$, and other derivatives, are sold under special trade names. They are high in the *ortho* compound because of trade demand for the *para* isomer.

Toluene, toluol, or **methylbenzene,** $CH_3C_6H_5$, is a colorless inflammable liquid prepared by fractional distillation of the light oil fraction of coal tar, or by extraction from illuminating gas. It is insoluble in water but miscible with alcohol or ether. The pure material boils at about 110°C. **Nitration pure toluene** boils within a range of 2°C. A second quality or **industrial pure toluene** is of but little lower quality and boils within a range of 4°C. Analagous to benzene, a solvent grade is sometimes offered boiling between 100° and 150° C. This is, strictly speaking, hardly toluene. Toluene is used in organic synthesis for the preparation of many compounds, and as a solvent closely related to benzene but less toxic. When nitrated it gives the explosive **trinitrotoluene,** popularly known as **TNT.**

Benzyl chloride, $C_6H_5CH_2Cl$, is a colorless, refractive liquid miscible with alcohol or ether. It is prepared by passing chlorine through boiling toluene until it has increased 38 per cent in weight. The product is washed with water and purified by fractional distillation. Both a 95-97 per cent refined grade and a technical product are available. It is used in making dyes and intermediates, perfumes, pharmaceuticals and synthetic resins.

Xylene, xylol, or **dimethyl benzene,** $C_6H_4(CH_3)_2$, is a colorless inflammable liquid containing a mixture of the three possible isomers, obtained by the fractional distillation of coal-tar naphtha. It is very soluble in alcohol or ether but insoluble in water. The isomers do not have identical boiling points, but boil within a range of about 6°C. Grades sold are 5° and 10° meaning that the distillation is cut within that range of temperature, and commercial. The **5° xylene** boils between 137° and 142° C. and is high in the *meta* isomer. The **10° xylene** boils between 135° and 145°C. The industrial grade differs but little from solvent naphtha, distilling only 90 per cent below 150°C. but completely below 160°C. Xylene is used in organic synthesis, sometimes after partial separation of the isomers, and as a solvent.

Solvent naphtha or **coal-tar naphtha** is a term for fractions of coal-tar distillate containing mixed hydrocarbons. Small amounts of benzene and toluene and large amounts of xylenes are present, with cumene and higher molecular-weight homologues. They are of white to straw color according to the degree of refining. The usual grades are water-white and high-flash, the latter being higher in price and stripped of the lower homologues. The flash point is over 80°C. and from a fire-risk viewpoint these solvents are considered relatively safe. Cuts are usually approximately 163-177°, 148-190° and 147-200°C. Uses as a solvent are in rubber products, in the preparation of synthetics, and in paints, varnishes, enamels and lacquers as a high-boiling hydrocarbon. The solvent properties are those of other coal-tar hydrocarbons but with a lower degree of volatility than benzene, toluene or xylene. They are closely allied to industrial grades of toluene and xylene, being simply higher in the content of the higher molecular-weight hydrocarbons. **Cumene** is also sold as a fraction cut within a range of 15° as a purified high-flash solvent. **Crude solvent naphthas** are sold with relatively wide distillation ranges. **Plasticizing oil** is a term for cuts of this nature distilling over 300°C. but having coal-tar hydrocarbon properties.

Shingle-stain oil contains high-boiling, crude coal-tar hydrocarbons. It distils between 140° and 350°C. and is dark red in color. It is designed as a solvent for wood stains, and as a solvent in baking enamels and other finishes where such a high boiling point is permissible. It is low in price.

Styrene, styrol or **vinylbenzene,** $C_6H_5CH:CH_2$, is a colorless to yellowish viscous liquid. It is present in storax and synthesized from cinnamic acid. The hydrocarbon is soluble in alcohol or ether and polymerized to a glassy resin, ***meta*-styrene** or ***m*-styrene.** The bromine derivative, **bromostyrene** or **dibromostyrene,** $C_6H_5CHBrCH_2Br$, also liquid, is an odorant of the hyacinth type used in perfumes and soaps.

Naphthalene, $C_{10}H_8$, is a white crystalline solid obtained by cooling the middle oil of coal tar or by other means described under coal tar. A crude grade is brown, due to incomplete removal of other constituents. It has the characteristic odor of "moth balls" and is insoluble in water, moderately soluble in absolute alcohol and very soluble in benzene. Grades sold are domestic crude of 74° and 78°C. melting point, and imported. It is also sold in a refined grade as balls, flakes, chips and crystals. It is used as an insecticide, particularly as a moth killer, and in organic synthesis. Because the color of dyestuffs is related to molecular weight this large molecule is particularly important in their synthesis. Derivatives of naphthalene are necessarily formed as intermediate products.

Synthetic naphthalene derivatives, such as **amylnaphthalene** or **monoamylnaphthalene,** $C_{10}H_7C_5H_{11}$, **diamylnaphthalene,** $C_{10}H_6(C_5H_{11})_2$, and mixtures with higher isomers are available. They are yellow to brown unless highly refined, are themselves mixtures of amyl isomers, and are the product of reaction of naphthalene and amyl chlorides in the presence of aluminum chloride. They are solvents and plasticizers.

Other high molecular-weight hydrocarbons of lesser importance than naphthalene are derived from coal tar, such as **anthracene,** $C_6H_4(CH)_2C_6H_4$; an isomer of anthracene, **phenanthrene; fluorene,** $(C_6H_4)_2:CH_2$, etc. Anthracene is available as an 80 per cent grade at a high price, and as a relatively inexpensive 40 per cent grade.

Tetralin or **tetralene** is **1,2,3,4-tetrahydronaphthalene,** $C_{10}H_{12}$, a colorless oil obtained by the hydrogenation of naphthalene at 150° C. in the presence of a catalyst. Commercially, decahydronaphthalene is usually present. Tetralin is insoluble in water but miscible with alcohol or ether, and is used as a solvent for naphthalene, rubber, waxes, resins, printing ink, etc.

Cymene occurs as three isomers but the commercial product is *para*-**cymene,** $CH_3C_6H_4C_3H_7$, *para*-**isopropyl toluene.** This is a colorless liquid having a pleasant odor, obtained by heating camphor with phosphorus pentoxide. It occurs in oil of cumin, wild thyme, lemon and other essential oils. Commercially it is obtained from camphor by heating with phosphorus pentoxide. In a less pure form it is a mixture of isomers and homologues obtained in the naval-stores industry. It has an aromatic odor, and is soluble in ether or chloroform and very soluble in alcohol. A refined grade is sold for use in organic synthesis, as a solvent, and as a basis for plastics.

Pine oil is the term for a class of very light yellow to deep yellow liquids of medium viscosity and varying but related odors. They are obtained by destructive distillation or by the steam distillation of pine wood. Pine oil is soluble in acetone, alcohol, chloroform, benzene, and turpentine but insoluble in water. Several fractions of lower viscosity are closely related to pine oil but sold under trade names. All are largely of terpene nature. Grades sold are destructively distilled and steam distilled. The latter has a more pleasant odor and is lighter in color. Uses are diverse, in paints and varnishes, soaps, disinfectants of the pine-oil type, textile-scouring preparations, ore flotation, degumming silk, general detergents, and as an odorant in many products. Pine oil is not to be confused with pine-needle oil, a more expensive odorant of terpene origin, nor with pine-tar oil, a phenolic type of product.

Terebene is a colorless mixture of turpentine hydrocarbons, chiefly dipentene and terpinene, prepared from oil of turpentine. The odor is somewhat like that of thyme, and the material resinifies on long exposure to light and air. It is a U.S.P. product with general properties as described, miscible with ether, chloroform, or absolute alcohol, and is used in medicine as an expectorant and antiseptic. It is relatively expensive and therefore not an industrial solvent. Related fractions sold under trade names are less expensive, and are used as solvents.

CHAPTER XVIII

PETROLEUM HYDROCARBONS AND RELATED PRODUCTS

The hydrocarbons derived from petroleum are numerous and complex, varying from natural gas and highly volatile and inflammable hydrocarbons to asphalts and wax-like bodies. In general they are derived from the same liquid source, crude oil or crude petroleum, with the qualification that petroleum from different sources varies greatly. A few are mined. As a general method of classification after consideration of the crude natural petroleum, the products have been considered roughly in order of decreasing volatility. At one time the products of petroleum were separated sequentially by distillation, as petroleum ether, gasoline, kerosene, safety kerosene or 300°-oil, light spindle oil, various grades of lubricants or gas oil, and fuel oil. The complexities of the industry no longer permit such simple and rational classification. They are in general unreactive. Some unsaturated hydrocarbons from natural gas or from the processing of petroleum have been considered with their derivatives in the preceding chapter.

The handling of petroleum products entails such a myriad of specifications that only a few can be discussed here, those most frequently used as reference points in quoting.

Varied special methods of testing petroleum products include the following: The **flash point** of an inflammable liquid is the temperature at which it evaporates at such a rate that its vapor forms an inflammable mixture with air under specified conditions, either with open-cup or closed-cup equipment. The **fire point** is the temperature at which the vapors collect fast enough to burn continuously under standard conditions with an open cup. Heavy oils such as lubricating oils are frequently classed by **viscosity.** This is usually reported as the Saybolt viscosity, the time in seconds required for 20 cc. of oil to flow through a standard orifice at a specified temperature. The temperature at which an oil will show a cloud is called the **cloud point.** The lowest temperature at which it will flow in a 4-ounce oil bottle is the **pour point,** sometimes referred to as the **cold test.** Lubricating oils are also classified by a **color number,** a value obtained by comparing the oil with a standard glass or a standard oil in a suitable instrument. **Specific gravity** of liquid petroleum products is usually reported in degrees Baumé.

Some products not of petroleum origin compete so directly with petroleum derivatives that they are also included in this chapter. The solubilities of petroleum derivatives do not differ sufficiently from product to product to justify repetition. In general, petroleum products are soluble in alcohol, benzene, chloroform or ether, the extent of the solubility varying in different fractions and also with the type of crude oil from which the material was derived.

Crude petroleum or **crude oil** is an oily liquid occurring in numerous shale and sandstone deposits throughout the world. While widely distributed, the two largest sources are the United States and Russia. Petroleum is thought by many to be organic in origin, possibly formed from the decomposed residues of plankton and similar microorganisms. Others postulate an inorganic synthesis of the hydrocarbons. Wells were originally drilled at points where petroleum has been found to accumulate. Deposits are now often located without any surface indications of oil seepage. The oil is forced to the surface of the earth by pressure of the gas which occurs with it. After wells cease to flow by gas pressure, the petroleum is pumped.

The physical properties vary widely even in the United States, where a California field gives a petroleum which is largely volatile enough for use as gasoline, another field a product more closely approaching asphalt in its crude form.

The orange to greenish brown or black liquid contains a multitude of hydrocarbons—open-chain, saturated and unsaturated, and cyclic. Open-chain saturated hydrocarbons varying from methane, CH_4, to one with a composition of $C_{27}H_{56}$, have been isolated from petroleum and the accompanying natural gas. They are sometimes designated the paraffin series of hydrocarbons. Sulfur and nitrogen compounds of an organic nature, considered as impurities, are usually also present. Petroleum varies in composition with the location of its source, but may be classified as either paraffin-base or asphalt-base in type. The former yields a crystalline solid, paraffin, consisting of compounds having the general formula, C_nH_{2n+2}. The latter yields noncrystalline material consisting of naphthenes, C_nH_{2n}, a series of saturated cyclic hydrocarbons. Some deposits are mixtures of the two types. Crude petroleum is quoted by the district in which it is produced such as California, Canada, Central West, East Texas, Gulf Coast, Kentucky-Tennessee, Louisiana-Arkansas, Mexico, Midcontinental, Pennsylvania, Rocky Mountain, South, Central and Southwestern Texas, Texas Panhandle, West Texas. Many of these are subclassed by dozens of divisions of the field.

Natural gas, occurring with the petroleum and derived from the same source, must be considered as a part of the petroleum. It is composed of volatile hydrocarbons, being a fraction which is gaseous at room temperature and a pressure of one atmosphere.

Methane, CH_4, is the major ingredient of natural gas, together with other higher boiling hydrocarbons. It is a colorless, odorless gas at ordinary temperatures. The natural gas is usually stripped of the condensable hydrocarbons by carbon treatment, use of silica gel, chilling or other processes to give casing-head gasoline. The remaining gas is piped and sold as fuel, used to enrich water-gas, burned in the production of carbon black or, in some fields, allowed to escape into the air to the extent of billions of cubic feet annually. **Ethane,** C_2H_6, is a colorless, odorless gas, present to some extent in natural gas. Neither methane nor ethane is quoted as such. Both are unreactive, so that derivatives are not made from them directly. Both are also major constituents of coal gas, produced by the distillation of coal for addition to water gas. Ethane is used to some extent as a fuel for dirigibles because the density of the gas approximates that of air, therefore the lifting power is not increased or decreased as it is consumed.

Propane, C_3H_8, is one of the most volatile ingredients of casing-head gasoline, so volatile that its presence is undesirable. It boils at −48.1° F. and is present in solution in the other hydrocarbons rather than as a true condensate. Propane is sold at a low price in cylinders under pressure, for use as gas where piped supplies are not available. No high degree of purification from other hydrocarbons is necessary. Some is used as a refrigerating medium, competing in a minor way with methyl chloride and ammonia.

Butanes, C_4H_{10}, are a mixture of the normal and isobutyl compounds, a product of natural gas boiling at 16-32° F. The properties and uses are in general similar to those of propane, with in addition some use as a very low-boiling solvent. A mixture containing much pentane is sold in steel cylinders and pressure tank cars for use as a gas supply where natural or manufactured gas is not available.

Normal pentane, $CH_3(CH_2)_3CH_3$, is obtained as a fractional distillate from casing-head gasoline. The colorless inflammable liquid is sold as a technical grade boiling at 28-38° C., and as a laboratory grade. It is used as an anesthetic and as a very low-boiling solvent. **Isopentane, or 2-methyl butane,** $CH_3CH_2CH(CH_3)_2$, is similarly derived and boils at 26-30° C. Its uses are similar but it is much more expensive, as would be expected from the closer cut. Impure pentanes are also present with propane and butanes in casing-head gasoline.

Hexane, C_6H_{14}, is a colorless liquid obtained by the fractional distillation of casing-head gasoline. A technical grade boiling at 60-70° C., a more closely cut fraction boiling at 65-67° C., and laboratory grades, are sold for use as a solvent. **Heptane,** C_7H_{16}, is similar to hexane in nature and source. Fractions sold are mixtures of various heptanes, and boil at 77-115° C., and at 86-100° C. **Octane,** C_8H_{18}, is similar to heptane and hexane. The commercial mixture boils at 100-140° C. and is used as a solvent.

Petroleum ether, petroleum spirit or ligroin, is a general term for low-boiling petroleum solvent. The term includes products boiling below room temperature in some cases. The composition varies with the boiling point, hydrocarbons from butane to octane predominating. In general, the grades sold are those boiling at 30-60°C., 55-60°C., 40-75°C. and a laboratory grade. It is used as a solvent, particularly for fatty materials. The term **benzine** usually means this class of solvent, but the term is sometimes more broadly used to include less volatile solvents.

Rubber solvent is a grade of petroleum ether especially refined for preparing solutions of crude rubber commercially known as **rubber cements.** It is classified by the constants obtained in distillation, as standard grade, 180°F. initial boiling point, 288°F. end point; and light grade, 120°F. initial boiling point, 250°F. end point. The standard grade approximates a grade sometimes called **benzene substitute.**

Naphtha is a term which is often applied to volatile petroleum fractions. It has no definite meaning unless modified by a qualifying term. Unqualified, it may mean anything from the lowest boiling petroleum ether to kerosene.

Varnishmakers' and painters' naphtha or **VM. and P naphtha** is a grade of petroleum distillate prepared as a highly volatile thinner for paint and varnish. Grades quoted are classified as 54-57° Bé., 190°F. initial boiling point, 310°F. end point; and 46.5° Bé., 254°F. initial boiling point, 380°F. end point. Many commercial grades are cut more closely than this. It has many miscellaneous uses.

Hydrogenated naphtha is a type produced by the hydrogenation of petroleum. It contains some cyclic-type hydrocarbons which modify the solvent properties. Grades are sold by numbers 1 to 4 for use as solvent for various purposes, largely in products used as protective coatings.

High-solvency naphthas are hydrocarbons of high cyclic-hydrocarbon content. They may be produced from petroleums containing upward of 18 per cent of cyclic compounds, by extraction with liquid sulfur dioxide, or by synthetic processes from petroleum hydrocarbons. **Toluene substitute** distils at 200-275°F. and contains over 70 per cent of cyclic compounds, **xylene substitute** at 275-370°F. and contains over 90 per cent. Varied grades are sold by number.

Stoddard solvent is a well recognized and defined fraction of petroleum. It has been called **safety solvent** and is sold by all major oil companies under various names. The specification drawn up in 1928 and revised in 1937 requires freedom from water and suspended matter, color not darker than 21 Saybolt which is water-white, sweet odor, flash point over 100°F. and in practice usually about 103°F., only slight corrosion of copper in 3 hours at 212°F., distillation of 50 per cent below 350°F., 90 per cent below 375°F., and an end point not over 410°F., and no acidity of the residue in the flask. It is normally quoted as specification CS3-37 which is that summarized in this paragraph. Stoddard solvent is intended for use in dry cleaning of fabrics—to avoid the fires in dry-cleaning establishments so prevalent a decade ago, when a more readily inflammable liquid was used. **Cleaners' naphtha** is very similar, but cut somewhat closer and correspondingly is somewhat more expensive.

Petroleum thinner or **turpentine substitute** is a closely cut fraction of petroleum distillate usually quoted by gravity in Baumé degrees, and by distillation range. Representative grades are 34°Bé., 325°F. initial boiling point, 390°F. end point; 44°Bé., 311°F. initial boiling point, 385°F. end point; 56°Bé., 200°F. initial boiling point, 300°F. end point; 43-47°Bé.; 47-49°Bé., etc. Varied grades are used as thinners in paints and varnishes, either as the light volatile diluent or for addition to the varnish in the kettle to "quench" it.

Lacquer diluents are petroleum fractions added to such an extent as is possible, in place of more expensive organic solvents. The dilution ratio of a lacquer solvent is a specific function of the solvent used. The use of the cheaper petroleum diluents permits lower cost of lacquers—too much diluent precipitates the cellulose derivative, either initially or during drying. From the latter statement it follows that the diluent must be more volatile than the solvent. Typical grades are classified as the following: Gravity 49-51°Bé., 257°F. initial boiling point, 365°F. end point; gravity 58-62°Bé., 160°F. initial boiling point, 270°F. end point; gravity 61-63°Bé., 149°F. initial boiling point, 275°F. end point. These liquids are closely related to other petroleum fractions used for other purposes.

Gasoline or **gasolene,** is a term which has evolved through various meanings as applying to volatile fractions of petroleum. **Straight-run gasoline** is that distilled directly from crude oil, usually between 200°F. and 400°F. **Cracked gasoline** is that obtained by application of various heating processes by which higher molecular-weight hydrocarbons are broken down to molecular weights of the size requisite for gasoline volatility. The same process produces many unsaturated hydrocarbons. **Casing-head gasoline** or **natural gasoline** is that recovered from natural gas by absorption in carbon black or activated carbon, by compression or by other methods. **Leaded gasoline** is that to which tetraethyl lead has been added to reduce the tendency to "knock" or "ping". **Antiknock gasoline** is that with a high antiknock value whether due to the presence of tetraethyl lead or to benzene or to unsaturated hydrocarbons. **Re-formed gasoline** is that produced by polymerization of gaseous hydrocarbons.

It is requisite that gasoline be sufficiently volatile to give off inflammable vapors below the average outdoor temperature, although it is relatively nonvolatile at 0°F. and below. The most important grading is by antiknock value expressed as octane number. This indicates its detonation characteristics, expressed as relative values in terms of a standard fuel. The standard fuel is a mixture of *n*-heptane and isooctane, (2,2,4-trimethyl pentane). The **octane number** of a motor fuel is the per cent by volume of isooctane that must be mixed with normal heptane in order to match the knock intensity of the fuel being tested. The higher the octane number, the less the tendency of the fuel to knock. Grades are available from 52 to 100, the latter being a special aviation gasoline. A maximum standard for sulfur-content is often specified, that of the U. S. government being 0.1 per cent.

The gravity normally varies from 52-78°Bé., the lower values being those of gasolines of higher volatility. Occasionally it is defined in pounds pressure per square inch at a given temperature, which is a measure of volatility by a static method, this being applied to natural gasolines where high pressure is disadvantageous, and therefore resulting in a lower price. Grading by initial boiling point and end point is common. The commercial grades are so complex that they can only be indicated in general. Pennsylvania grades are 60 octane; 52-54 octane, 450° F. end point; and 54-56 octane, 400° F. end point.

Kerosene, once of great importance for illuminating purposes, is a petroleum fraction of relatively minor significance, a fraction of lower volatility than gasoline. It is usually a straight-run product from the distillation of crude oil. Kerosene is graded by color as prime white, water white, etc. and by specific gravity, such as 41-43°Bé., 42-44°Bé., 45°, 46°, and 47°Bé. It is used as an illuminating oil and as a burning oil in stoves. Some minor amounts are used as solvents and some solvents already discussed are fractions obtained from kerosene by redistillation into closely cut fractions. **Deodorized kerosene** is a more highly refined grade, usually treated with activated earth or carbon. It is used as a vehicle for insect sprays, usually containing pyrethrins from pyrethrum flowers.

Furnace oil or **kerosene distillate** is a petroleum distillate having a specific gravity of the order of 40°Bé. It is usually sold by number from 1 to 4, No. 1 being the most expensive, but occasionally by specific gravity, such as 28-30°Bé., 32-36°Bé., 36-38°Bé. and 38-40°Bé., and by color, such as straw and light straw. This oil fraction is used in furnaces equipped with a simple vaporizing burner and is best visualized as a low-volatility kerosene.

Gas oil usually consists of the last fraction distilled from petroleum, the highest-boiling fraction. The yellow to brown oil is sold according to source by specific gravity, usually 32-36°Bé. It is used for the production of gas by spraying on hot brick work in a "carburetor". This gas is then added to water gas to increase its value for illumination and heating.

Fuel oil varies widely in composition, but is usually the hydrocarbon residue distilled after the lighter products have been separated from petroleum by distillation up to a temperature of about 575°F. It is sold by specific gravity expressed in degrees Baumé, such as 16-20°, 24-26°, 26-30°, etc. In some cases a cold test is specified such as 0°F. or 15°F. High-grade fuel oil is sold as **Diesel oil** for use in the Diesel type of internal combustion engine. Other grades of burner oil are used for steam generation, as in the oil-fired power boilers of factories, locomotives, steamships, etc. A less common grade is not distilled but constitutes the residue after gasoline distillation and is called **residual fuel oil.**

Paraffin oil is a fraction distilled from the fuel oil fraction of petroleum after the wax has been separated by cooling and filtration. The yellow to brown oil is usually treated with sulfuric acid and with adsorbent earth to give a light-colored oil relatively free from impurities. It usually has a flash point varying from 320°F. to 360°F. and a viscosity varying from 60 to 110 seconds Saybolt. It is used for varied purposes such as in leather dressing, floor treatment, etc. or, if further refined, as a lubricant.

Putty oil is a petroleum fraction added to putty to serve as a lubricant and softener, to avoid its becoming too hard after drying of the linseed oil vehicle. A typical oil is of 34°Bé., viscosity about 80 seconds Saybolt at 100°F.

Lubricating oil is a general class of oil having many subclasses. **Spindle oil** is a very light grade, **machine oil** a heavier class. **Cylinder oil** is a heavy-duty grade. For lubrication of automotive engines, grades of light, medium and heavy are sometimes specified. Other classifications are by **SAE values** according to specifications of the Society of Automotive Engineers. Grades from Pennsylvania crude are superior in lubricating value to those distilled from naphthenic crudes and are usually specially designated. Paraffinic hydrocarbons are also separated from naphthenes by solvent extraction, such as by nitrobenzene. Such oils are believed to be identical in performance with straight paraffin oils. Some lubricating oils are artificially colored with fluorescent dyestuffs. The change in viscosity with change in temperature is important and is obtained by calculation from the Saybolt viscosity at 100° F. and at 212° F. It is designated as the **viscosity index.**

Methods of recovery and refining are numerous. Light grades are distilled, heavier grades are recovered from the residue after distilling light fractions. Standard treatment has been to chill to remove paraffin, treat with sulfuric acid to remove unsaturated bodies, and filter through activated forms of mineral earth to clarify and bleach. These methods of refining are constantly undergoing modification.

Systems of quoting grades can only be briefly suggested. Lubricating oils are quoted by viscosity, by colors in the Union Colorimeter, or color numbers of the American Petroleum Institute. They are classed as bright stock, meaning that paraffin has been removed by chilling, as neutral oils, by pour test, etc. Even a number of pages of classes available could hardly cover the varied grades. Uses vary from lubrication of sewing machines to that of steam locomotives, from preventing rusting of small parts to coating machinery for protection during storage.

Transformer oil is a substantially nonvolatile grade of mineral distillate carefully freed from water, acids, etc., and used as a cooling agent in transformers, for conduction of heat, and to improve the insulation characteristics.

White mineral oil, white oil or **liquid paraffin** is obtained from the fraction of petroleum distilling at 626-734°F. The distillate is purified by various methods. A typical procedure is treatment with sulfuric acid, washing with water, treatment with caustic soda, washing, and hot filtration through activated carbon to remove all color. The resulting oil is cooled, separated from the solid material and redistilled. The fraction which distils above 680°F. is the usual white mineral oil. Technical grades of the domestic product vary in Saybolt viscosity from 50 to 90; U.S.P. grades vary in viscosity from 80 to 345. The Russian oil ranges in viscosity from 75 to 345. Quotations usually cover a range of 10 seconds viscosity. White mineral oil is mainly used medicinally as a laxative. There are however, varied miscellaneous uses to which it is applied.

Petrolatum or **petroleum jelly** is obtained by suitable treatment of the residues left in paraffin-base petroleum after other fractions have been separated by steam distillation. It is frequently spoken of by a trade name, **Vaseline.** It consists mainly of both saturated and unsaturated hydrocarbons of the paraffin series. Petrolatum forms a jelly-like, oily, semi-solid mass which melts on gentle warming. Grades sold are mostly by color, such as dark, medium and light amber, dark green, red, cream white, lily white, snow white. There is also a veterinary grade. U.S.P. petrolatum melts at 38-54°C. White petrolatum is obtained by bleaching the dark crude product, melting and filtering through decolorizing carbon. This processing alters other properties. Petrolatum is used medicinally as the base of many ointments and has a multitude of other miscellaneous uses.

Lubricating greases are sold of varying consistencies. While of petroleum origin the base is usually a fairly light oil thickened with sodium soap or heavy metal soaps such as those of calcium, aluminum, etc. The diverse requirements prevent adequate classification of the many types and uses.

Asphalt, asphaltum or **gum asphaltum** at one time was a bituminous material occurring naturally at Pitch Lake on the Island of Trinidad, probably produced by the partial oxidation and evaporation of petroleum. The term has been broadened by use so that it now includes many substances of an asphalt-like nature. It is obtained as a residue in some methods of refining petroleum, and spoken of as **petroleum pitch.** Besides hydrocarbons, some combined sulfur, oxygen and nitrogen are present, along with inorganic contamination such as of earthy material. Important grades are Barbadoes or Manjak A and AA; California; Cuban A and B; Egyptian; Gilsonite brilliant black, seconds and selects; Maltha; and Mexican. Grades used in rubber compounding are known as **mineral rubber.**

Asphalt comprises so many grades that the uses are diverse. It is used for paving without modification. Asphalt is used for waterproofing and for roofing, either as a plastic or applied in a solvent. Many compounded plastic materials, such as insulating compounds contain asphalt. When diluted to a liquid or semisolid with petroleum thinner it is known as **cut-back asphalt.** Emulsified in water with bentonite, soap or other emulsifier, it is sold as **asphalt emulsion.** These emulsions are used mainly for road building. **Asphalt paints** are an important article of commerce both for surface protection and for waterproofing. The asphalt is either emulsified in water or dissolved in suitable solvents.

Fatty-acid pitch or **stearin pitch** is a class of products obtained as a by-product residue in the refining of fats and oils, in the production of fatty acids, or in refining refuse greases. They are in properties largely analagous to complex hydrocarbons. The fatty-acid pitches available are of very diverse origins and are usually named by their source, such as **cottonseed pitch, linseed pitch, stearin pitch,** etc. The products are brown to black and contain a relatively high proportion of fixed carbon with some colloidal carbon and humins. On heating they have an odor of fatty acid. They are largely but not completely soluble in petroleum solvents, are of low price and compete with asphalts. They are used in the manufacture of tarred paper, black paints and varnishes, as an impregnating and insulating agent, for filling rubber, as a waterproofing agent, etc.

Wood-tar pitch is a hard, brittle material left as a residue from redistillation of the tar from the destructive distillation of wood. It is of the general nature of hydrocarbons, the active chemical materials having been distilled. This grade of pitch is partially to completely soluble in benzene and organic petroleum solvents. Hardwood and pine-tar pitches are sold. They are competitive with asphalt and are used in making dark-colored varnishes, fuel, roofing paper, as a preservative coating, in insulation, for calking seams, etc. Pine-tar pitch is more sticky in nature than other types of pitch, and is therefore used when that property is desired.

Paraffin or **paraffin wax** is a hydrocarbon mixture having the physical properties of a wax, and is obtained from the distillate from the fuel-oil fraction of petroleum, by chilling and filtering. The solid separated in this way is refined by pressing out the oil from the first grade or **scale wax,** and decolorizing with activated carbon or earth. The melting point is important in various uses to which it is put. Among the many grades are the following: Crude white scale melting at 122-4° or 124-6°; crude yellow scale melting at 124-6°;

semirefined solid melting at 124-6°; fully refined slabs melting at 123-5°, 125-7°, 128-30°, 130-32°, 133-5°, 135-7°, 138-40° and 143-5°, all in Fahrenheit. The price increases with refining and particularly with increase in melting point so that 143-5° melting-point material costs at least 50 per cent more than 123-5°. Match paraffin is a low-price grade melting at 105-15° F. Paraffin is used both in solid form and as an impregnating material, applications including candles, matches, lubricants, crayons, waxed paper, waterproofing of wood, insulation, phonograph records, floor waxes, and nonreactive coatings.

Ozokerite consists mostly of solid paraffin hydrocarbons. It occurs naturally, the principal deposit being in central Europe. It is thought to result from the evaporation of petroleum. Ozokerite is purified by melting with hot water and separating the wax from the earthy material. The crude wax is greenish brown to black. It is bleached by melting with activated carbon and is sold largely by melting point. The grades are hard green, with congealing points of 66-68°C., 70°C. and 74°C.; yellow 76-8° C.; and snow-white 76-8° C. All grades of true ozokerite are expensive. It is used in candles, paints, electric insulation, printing inks, floor polishes, etc., as a rubber filler, and for making ceresin.

Ceresin is a non-crystalline, wax-like product. It is often thought that it is obtained by purifying ozokerite by treatment with sulfuric acid, followed by washing and neutralization. Actually much paraffin and other wax-like material of mineral origin is incorporated in commercial ceresin as indicated by the price, which is of the order of one-fourth that of crude ozokerite. Bleached ozokerite is sold as such instead of as ceresin. Grades of ceresin sold melt at 138-40°F., 150-60°F. and over 160°F. It is used much the same as beeswax, in shoe polish, floor wax, candles, sizing agents, leather dressing, etc.

Montan wax is a high-melting wax-like solid composition prepared by extraction of bitumen from lignites. **Crude montan wax** is a dark brown material varying in composition, but usually containing esters of montanic acid along with a major content of hydrocarbons. It can be bleached to a light-colored grade, and is soluble in chloroform, carbon tetrachloride, benzene and many grades of petroleum solvent. The melting point is usually about 80-90°C. It is related to the petroleum hydrocarbons rather than the true waxes, although used as a substitute for the latter in many of its applications. Montan wax is used in making polishes, candles, phonograph records, paper-sizing compositions, paints, electrical insulating compositions, adhesives, etc.

CHAPTER XIX

ALCOHOLS

Alcohols are organic compounds characterized by the presence of the hydroxyl group. The hydrogen of the hydroxyl group may react to form new compounds as in the formation of alcoholates or the hydroxyl group may react as a whole as in the formation of esters. The organic radical may be very simple as in methyl alcohol, or highly complex as in geraniol. It may be saturated or unsaturated, straight chain or cyclic. If cyclic, the hydroxyl group occurs in the side chain. Aromatic compounds which have a hydroxyl group attached to a ring carbon atom are phenols. These differ in properties from alcohols. An alcohol may contain more than one hydroxyl group, such as glycol with two, and glycerol with three. Scientific usage attaches the "ol" ending to indicate that a compound is chemically an hydroxyl derivative, although industrial usage frequently ignores this, as in using the term "glycerine" instead of "glycerol".

The most common alcohol, ethyl alcohol, is next in importance to water as a solvent and may be said to occupy the same position in organic chemistry as water does in inorganic chemistry. When only alcohol is specified ethyl alcohol is meant. The subject is complicated by the fact that the same compound may be an alcohol and an acid, or an ether and an alcohol, or may contain even more complex combinations. In classifying these mixed types of compounds, they have been placed according to the chemical property which appears most important in the major use of the material.

The carbinol type of nomenclature is based on representing alcohols as substituted methyl alcohols. Thus methyl alcohol is carbinol, CH_3OH, methyl carbinol is CH_3CH_2OH, one hydrogen being replaced by CH_3. Similarly, dimethyl carbinol is $(CH_3)_2CHOH$, trimethyl carbinol $(CH_3)_3COH$, and methyl propyl carbinol $(CH_3)(C_3H_7)CHOH$.

Methyl alcohol, methanol, wood alcohol or **wood spirit,** CH_3OH, is the simplest possible representative of the alcohol class, and is miscible with water, alcohol or ether. It is a colorless, limpid liquid. A characteristic odor usually associated with it is largely due to impurities, and modified but not eliminated when the alcohol is pure. The historic method of manufacture perpetuated in the name wood spirit, is by destructive distillation of wood. The distillate also contains acetic acid, acetone and methyl acetate. After neutralizing the organic acids with lime, the liquid is again distilled, dried by treatment with calcium chloride and fractionally redistilled to separate other volatile substances present. The major modern method of preparation is from carbon monoxide by reaction with hydrogen under pressure in the presence of a catalyst, said to be composed of zinc oxide and chromic acid. Higher alcohols and water are produced at the same time but methyl alcohol can be separated from these by fractional distillation.

Grades sold are natural crude; denaturing grade; pure, natural or synthetic; 97 per cent, natural or synthetic; and 95 per cent, natural or synthetic. The pure is normally guaranteed to be over 99.5 per cent. The balance in all cases is largely water. A definite trend to the use of the term methanol rather than methyl alcohol or wood alcohol is encouraged in the trade, to avoid confusion with alcohol, meaning ethyl alcohol. Because of its poisonous nature, methanol is a major denaturant for ethyl alcohol to render it nonpotable and therefore tax-free. Methyl alcohol is more expensive than tax-free ethyl alcohol but does not have the government restrictions that hamper the user of the latter. Therefore it is frequently substituted as a solvent where possible. It is a raw material for the manufacture of formaldehyde and many synthetic organic chemicals. A minor use is as a fuel. Another important application is as a radiator anti-freeze, where it replaces a greater weight of ethyl alcohol required for an equivalent lowering of the freezing point.

Ethyl alcohol, alcohol or **ethanol,** C_2H_5OH, is a clear colorless liquid of characteristic odor when pure, miscible with water and ether. Commercially it is produced in enormous quantities from molasses, a by-product of the sugar industry. This is fermented with yeast, and is classed as **molasses alcohol,** from its source. Alcohol is also produced by fermentation of starch from grain, and called **grain alcohol.** This term is sometimes incorrectly used as a synonym for ethyl alcohol, regardless of source. The fermentation yields as a by-product a spent mash which is high in proteins, containing nearly all of the protein of the original grain. In the process the starch is first hydrolyzed to sugars by the yeast, and these are acted on by another ferment of the yeast to form alcohol and carbon dioxide. Therefore the industry is a major source of supply of the by-product, carbon dioxide. Alcohol has been produced by hydrolysis of wood cellulose with acid to form sugars, which are then fermented. Synthetic ethyl alcohol has also been produced by the catalytic union of ethylene and water. In all cases it is purified by fractional distillation, sometimes also by treatment with activated carbon. Distillation through an efficient fractionating column yields a constant-boiling mixture with water, containing 95 per cent of alcohol and 5 per cent of water by volume. This may be refined to absolute alcohol by adding benzene and distilling, a ternary benzene-alcohol-water compound being separated in the distillation. Grading is on a basis of the proof gallon which contains 50 per cent of water and 50 per cent of alcohol by volume. Thus **absolute alcohol** or **anhydrous alcohol** is 200 proof, or 100 per cent pure ethyl alcohol.

Alcohol is quoted as 190 proof, and absolute, with the additional designation as from grain, from molasses or synthetic. This designation of the source is not because of distinguishable differences in the product, although salesmen for alcohol sometimes contend that such differences are detectable, but because of government restrictions. The U.S.P. grades for these concentrations correspond to not less than 94.9 per cent by volume at 15.5° C. for the ordinary grade, and not less than 99 per cent by weight for the absolute. Grain alcohol commands a premium and the law requires that it be used in manufacture of potable beverages. The use of alcohol is hedged about with many governmental restrictions as to permits. While inherently not a very expensive material, when not denatured, ethyl alcohol is subject to a tax which is often 90 per cent of the selling price, which makes it expensive.

Tax-paid alcohol is used in making **flavoring extracts,** which are usually alcoholic solutions of essential oils or other flavoring ingredients. It is used in perfumes and in many medicines. The term **tincture** is used to differentiate an alcoholic extract for medical use from solutions in other solvents. Other important uses are in organic synthesis, for the manufacture of celluloid and other plastics, in antiseptics and disinfectants, as a solvent for gums, particularly shellac, and in general as the solvent for organic substances, much as water is a solvent for inorganic substances. Automobile-radiator antifreeze use consumes large volumes. Its use as a blend with gasoline as a motor fuel has made substantial progress in Europe and to a lesser extent in the United States. The anhydrous grade is necessary for this, and butyl alcohol must be added as a mutual solvent to prevent separation into layers in the presence of a small amount of water.

Nearly all **alcoholic beverages** are alcoholic solutions having characteristic tastes and aromas because the purification by distillation has intentionally not been complete. They are listed briefly because they are commercial forms of tax-paid alcohol. They are described without the detail of the legal definitions.

Whiskey is the alcohol at 85-100 proof, distilled from a fermented grain mash. **Rye whiskey** means that rye predominated in the mash, **corn whiskey** or **bourbon whiskey** that corn predominated. **Scotch whiskey** and **Irish whiskey** take their names from characteristic odors derived from peat smoke in preparation rather than from the raw materials. **Rum** is similarly produced from fermented molasses, at 85-100 proof. **Wine** is fermented grape juice, **brandy** the alcohol distilled from wine to a concentration of 90-100 proof. Wine will contain only 12-16 per cent of alcohol from fermentation, but **sherry, port** and **tokay** wines are fortified to 20-22 per cent, and occasionally even to 28 per cent with brandy or grain alcohol. **Beer** is a malt beverage containing 3.5-7 per cent of alcohol, to which the hops and processing give characteristic flavors.

Liqueurs of varied names are flavored syrups fortified with alcohol. **Gin** is made from alcohol by distillation through a mixture of herbs and berries in which juniper, coriander, etc., predominate, adjusted to 85-100 proof. Gin and the liqueurs are the only beverages made directly from alcohol, the others being unrefined or only partially refined alcohol.

Completely denatured alcohol is that to which materials have been added to make it objectionable as to odor and taste and therefore nonpotable. As an incidental factor it is made poisonous because that is the nature of the denaturants used. It is tax-free and no permit for its use is required.

Completely denatured alcohol has been prepared in the past with gasoline, wood alcohol, pyridine, etc. Formulas are changed rather frequently. The following are typical: Formula CD11 contains 3 gallons of Pontol K, 1 gallon of aviation gasoline, 0.5 gallon of Agdite or 1 gallon of Hydronol and 3 gallons of a preparation designated as ST115, per 100 gallons of alcohol. The denaturants added to CD12 are similar with an increase of Pontol K to 4 gallons and replacement of ST115 by 2 gallons of methyl isobutyl ketone. Formula CD13 differs from CD11 in increase of ST115 to 4 gallons and replacement of Pontol K by 2 gallons of methyl isobutyl ketone. The composition of the named denaturants is not generally known. Completely denatured alcohol is widely used as a solvent, as anti-freeze for automobile radiators, as a cleaning agent for metals in industrial plants, as a fuel, in cements, paint- and varnish removers, in spirit varnishes and in other products where no physiological application is possible. Completely denatured alcohol should not be used as a rubbing alcohol. For that purpose special denatured formula 23G is used with additions made by the bottler.

Special solvent-alcohol is a completely denatured and therefore tax-free grade. No permit is required. It may not be used for anti-freeze purposes. It is anhydrous and a typical formula contains 5 gallons of Tecsol, 2.5 gallons of Pontol K, 2.5 gallons of isopropyl alcohol and 0.5 gallon of aviation gasoline per 100 gallons of absolute alcohol. As the name indicates, it is used largely as a solvent for lacquer, resins, etc.

Specially denatured alcohol is permitted for use where completely denatured alcohol will not serve the purpose and where it is not intended for food, medicinal or beverage purposes. The denaturant added therefore depends on the application or the industry in which the alcohol is used. To obtain such alcohol it is necessary to have a permit, and if a substantial amount is required, to file a bond. Specially denatured alcohol is tax-free. It is sold as 190 proof and anhydrous. The following are examples of denaturants added to suit industrial applications for which large volumes are quoted. Formula SD1 contains 5 gallons of approved wood alcohol in 100 gallons of ethyl alcohol. Formula SD23G contains 10 gallons of U.S.P. acetone and 4.25 ounces of sucrose octoacetate in 100 gallons of ethyl alcohol. Special denatured alcohol formulas are numbered to 47, with some having as many as seven subformulas indicated by letter designation. Where alcohol is required for chemical purposes, a special denatured formula is ordinarily used. Formula SD1 is authorized for over 200 different uses, such as the manufacture of acetaldehyde and ether, making textile soaps, etc.

Propyl alcohol, C_3H_7OH, is the next member of the family above ethyl alcohol. **Normal propyl alcohol** is a straight-chain compound and is not available in quantity. The usual commercial product is **isopropyl alcohol** or **isopropanol,** $(CH_3)_2CHOH$, a colorless liquid having less odor than ethyl alcohol and of slightly higher boiling point. It mixes with water, alcohol and ether. The major source is by synthesis from natural gas, or from cracking gases from the oil industry, propylene being first obtained, this dissolved in sulfuric acid and the resulting unstable propyl hydrogen sulfate hydrolyzed with water. Acetone can be reduced by hydrogen at 120° C. with a nickel catalyst to give isopropyl alcohol. Various grades are denaturing, refined 91 per cent, refined 98 per cent, technical 91 per cent and technical 98 per cent. The balance in each case is largely water, the 91 per cent grade being a constant boiling mixture with 9 per cent of water. Isopropyl alcohol is used as a substitute for ethyl alcohol in many solvent applications to avoid the restrictions of alcohol permits, but cannot be so used in food products. Isopropyl alcohol is also used to form esters and other organic derivatives. It is only slightly more expensive than completely denatured alcohol.

Butyl alcohol, C_4H_9OH, has several structures. **Normal butyl alcohol,** $CH_3(CH_2)_2CH_2OH$, is a colorless liquid with a characteristic odor, moderately soluble in water and miscible with alcohol or ether. It is obtained when starch and sugars are fermented with a special bacillus, acetone being formed at the same time. It is also produced synthetically. Butyl alcohol is used as a solvent for resins and varnish gums, in the manufacture of lacquers, cleaning solutions, photographic films, plastics, and varnish removers. It is used for manufacture of esters and other derivatives. **Secondary butyl alcohol,** $CH_3CH_2CH(OH)CH_3$, is similar in solubility and other properties to normal butyl alcohol. It is prepared by the reduction of methylethyl ketone or by the reaction of normal butylene and sulfuric acid to form butyl hydrogen sulfate followed by hydrolysis to secondary butyl alcohol. Uses are as a solvent and in the manufacture of esters and other derivatives. **Isobutyl alcohol,** $(CH_3)_2CHCH_2OH$, is also similar in properties and uses. It is obtained by the fractional distillation of fusel oil, purified by rectification, and sold as a refined grade. **Tertiary butyl alcohol,** $(CH_3)_3COH$, is another but more expensive member of this group.

Amyl alcohol, $C_5H_{11}OH$, has many isomers. Either a natural mixture recovered from fusel oil or a synthetic mixture is sold under that name, the synthetic product being made by reaction of amylene with sulfuric acid to form amyl hydrogen sulfate, followed by hydrolysis. The natural mixture is a clear, colorless liquid of characteristic odor, distilling over a range of about 30° C. The synthetic mixture distils over a narrower range, about 20° C. Amyl alcohol is moderately soluble in water and mixes with alcohol or ether. It forms a constant-boiling mixture with water. Its uses are mainly in lacquers and for organic synthesis. Some is used as an antifoaming agent. The mixture is the major amyl alcohol available. A refined grade distills over a range of about 6° C. and contains about 85 per cent of isoamyl alcohol, the balance being other isomers.

Isoamyl alcohol, $(CH_3)_2CHCH_2CH_2OH$, is isolated from mixed amyl alcohols and used mainly for organic synthesis. **Normal amyl alcohol** or **normal butyl carbinol,** $CH_3(CH_2)_4OH$, is also available as a synthetic product. It distills over a much closer range than the mixture, but is used for similar purposes. **Secondary amyl alcohol,** $CH_3(CH_2)_2CH(OH)CH_3$, and **tertiary amyl alcohol,** $(CH_3)_2(C_2H_5)COH$, are also synthetic products of similar nature. These are sold at prices which permit their use as solvents. Others are available in purified form at prices which preclude their use other than for synthetic purposes. Some duplicate those already listed as solvents but differ in quality. The important ones are **normal amyl alcohol** or **normal butyl carbinol,** $CH_3(CH_2)_4OH$, **secondary amyl alcohol** or **secondary butyl carbinol,** $CH_3(CH_2)_2CH(OH)CH_3$, **diethyl carbinol,** $(C_2H_5)_2CHOH$, **isoamyl alcohol** or **isobutyl carbinol,** $(CH_3)_2CHCH_2CH_2OH$, **methyl propyl carbinol,** $(CH_3)(C_3H_7)CHOH$, and **dimethyl ethyl carbinol,** $(CH_3)_2(C_2H_5)CHOH$.

Fusel oil is present as an undesirable product in the alcoholic liquors produced by the fermentation of potato, corn and other carbohydrate mashes, and is separated as a by-product. It contains principally isoamyl alcohol, with varying amounts of other amyl alcohols except the normal one, other alcohols such as butyl and hexyl alcohols, and small amounts of fatty acids. The volatile oily liquid has a disagreeable odor. It is purified by distillation, and a refined grade is sold. Fusel oil is used for fractionation to isolate amyl compounds, as a solvent for oils, waxes and resins, and to a limited extent in lacquers.

Amyl mercaptan, amyl hydrosulfide or **amyl sulfhydrate,** $C_5H_{11}SH$, is structurally a thioalcohol, one in which oxygen has been replaced by sulfur. It is a colorless liquid, insoluble in water but miscible with alcohol or ether. It is prepared by the reaction of amyl iodide, $C_5H_{11}I$, with potassium hydrosulfide, KSH. The commercial product is a mixture of isomers in which **isoamyl mercaptan** predominates. The presence of the sulfur atom gives the compound a very disagreeable odor.

It is used as an intermediate in organic synthesis, as a flotation reagent, to give an obnoxious odor in stench bombs and is introduced into gas to permit ready detection of leaks.

Secondary hexyl alcohol, $CH_3(CH_2)_3CH(OH)CH_3$, is almost insoluble in water but miscible in all proportions with alcohol or ether. It is a colorless, oily liquid of pleasant odor when pure. Hexyl alcohol is recovered from fusel oil as a relatively inexpensive and nonvolatile solvent, and produced synthetically. Some is used for organic synthesis. An isomeric hexyl alcohol which is structurally **2-ethyl butyl alcohol,** $CH_3CH(C_2H_5)CH_2CH_2OH$, is similar in properties and uses.

Octyl alcohol, octylic alcohol, capryl alcohol, caprylic alcohol or **C-8 alcohol,** $CH_3(CH_2)_5CH(OH)CH_3$, is a secondary alcohol, a colorless, oily liquid. The odor is aromatic, with a rose tone, but tends to be waxy. It is soluble in water, miscible with alcohol or ether and is obtained by distilling castor oil with an excess of alkali, such as lime or caustic soda. It is also produced by reduction of the fatty acids derived from coconut oil. Pure and technical grades are sold. It is expensive and used in rose and jasmine perfumes, in organic synthesis, and as an antifoaming agent. Lower grades find a limited solvent use.

Higher alcohols than **octyl,** usually quite expensive, are derived from various sources, largely by reduction of the corresponding fatty acids, and used in perfumes. They are often named by their number of carbon atoms instead of by chemical names. This has no significance as to whether a straight-chain or branched-chain structure is present and may lead to the same term applying to structural isomers. **Nonylic alcohol, nonyl alcohol,** or **C-9 alcohol,** $C_9H_{19}OH$, is a colorless to light yellow liquid, soluble in water, miscible with alcohol or ether and used in orange and tuberose odors. The odor of the alcohol is rose-like. **Decylic alcohol, decyl alcohol,** or **C-10 alcohol,** $C_{10}H_{21}OH$, is a colorless to light yellow liquid, soluble in alcohol or ether. It is used in orange, neroli and violet odors. **Undecylic alcohol, undecyl alcohol,** or **C-11 alcohol,** $C_{11}H_{23}OH$, is similar but used for rose and lily odors. **Lauryl alcohol, lauric alcohol** or **C-12 alcohol,** $C_{12}H_{25}OH$, is used for tuberose odors. **Cetyl alcohol,** $CH_3(CH_2)_{14}CH_2OH$, is a waxy white to yellow solid, soluble in alcohol, chloroform or ether. It is obtained by saponification of spermaceti, and when pure has a rose-like odor. It is also obtainable by catalytic reduction of the corresponding fatty acid. Varied grades are sold, domestic C.P., domestic commercial, imported 85 per cent, and imported commercial. It is used in skin preparations, as a fixative in perfumes, for production of synthetic organic chemicals and for sulfation to give alkyl sulfates, used as detergents. The price varies with the grade, corresponding to the purpose for which the material is suitable.

Diacetone alcohol or **4-hydroxy-2-keto-4-dimethyl pentane,** $CH_3COCH_2C(CH_3)_2OH$, is a colorless liquid miscible with water, alcohol or ether. It is both a ketone and an alcohol, prepared synthetically. Diacetone alcohol is sold as pure, and as a technical grade which contains some acetone. It is a solvent for lacquers, plastics and resins, available at a price permitting its use as a solvent.

Ethylene glycol, $(CH_2OH)_2$, is miscible with water or alcohol and is prepared by heating ethylene dichloride or ethylene chlorohydrin with a suitable alkaline solution under pressure. It is the simplest polyhydric alcohol. The colorless syrupy liquid is hygroscopic. It is used as an antifreeze solution in automobile radiators, as a coolant in airplane engines, in the manufacture of explosives and for a great variety of purposes to replace glycerine in nonfood uses. For example, some brands of cigarettes use it or its derivatives as the hygroscopic agent in place of glycerine; it is quite widely used in cosmetics. The manufacture from it of **glycol dinitrate,** $(CH_2NO_2)_2$, as a substitute for nitroglycerine, replaces the by-product glycerine as a raw material with a synthetic product available in any reasonable amount.

Propylene glycol, $CH_3(CH_2OH)_2$, is closely related to ethylene glycol in preparation, properties and uses.

Diethylene glycol, $CH_2OHCH_2OCH_2CH_2OH$, is a colorless, syrupy, liquid, miscible with water and alcohol, and very hygroscopic. It is structurally an ether as well as an alcohol. The production is probably as a by-product in the manufacture of ethylene glycol, although it can be synthesized as a primary product. It is used as a solvent for nitrocellulose and gums, as a moistening and softening agent for glue, parchment paper, etc., in the printing of textiles, and in the manufacture of explosives. In these uses it largely replaces glycerine.

Triethylene glycol, $CH_2OH(CH_2OCH_2)_2CH_2OH$, is a colorless, hygroscopic liquid which is both an ether and an alcohol. It is soluble in water but immiscible with organic hydrocarbons. Commercially it is probably from by-product sources, and is usually contaminated with homologues. Uses are as a solvent for nitrocellulose and gums and as a plasticizer in varied applications. Derivatives have similar uses.

Ethylene chlorohydrin, CH_2ClCH_2OH, is both an alcohol and a halogen derivative, the stage intermediate between ethylene dichloride and ethylene glycol. It is produced by the reaction of ethylene and hydrogen chloride gas. The colorless liquid is miscible with water and is sold as a 40 per cent aqueous solution, which is close to the composition of its constant-boiling mixture with water. The anhydrous material is also available. Uses are largely in synthetic organic chemistry.

Glycerol or **glycerine,** $C_3H_5(OH)_3$, is a trihydric alcohol present in fats and fatty oils, where it is esterified with the higher aliphatic acids. It is a viscous liquid colorless when pure, miscible with water or alcohol, and is very hygroscopic. Glycerine is obtained from fats and saponifiable oils by hydrolysis. Soap-lye contains a high proportion of water, the salt with which the soap was salted out, impurities separated from the raw materials used in soap manufacture, residual lye and 3-5 per cent of glycerine. A higher concentration of glycerine is obtained when fats are split to give fatty acids by means of the Twitchell reagent. Crude glycerine is obtained from these by precipitating soap and other impurities with lime and concentrating to about 80 per cent glycerine. Refined glycerine is obtained by distillation. A 95 per cent glycerine free from solids is prepared by distillation under reduced pressure with superheated steam. The colorless product is obtained by treatment with charcoal to remove yellow coloring matter.

Glycerine which contains no impurity but moisture, is prepared by redistillation and treatment with activated carbon to give a C.P. grade. The U.S.P. grade is colorless and contains not less than 95 per cent of glycerine. Other grades sold are dynamite; saponification, basis 88 per cent; soap-lye, basis 80 per cent; and yellow distilled. Various grades are used in printer's inks, plastic clays, polishes, as an antifreeze when the price permits, in making nitroglycerine which absorbed in a carrier is dynamite, as a textile softener and solvent for textile chemicals, as a lubricant, in plastics, paper, ink, leather, etc., as a softener, in cosmetics, as a solvent for drugs and essential oils, as a moistening and flavoring agent in tobacco, as a preservative for foodstuffs, and in many similar ways. Because of its derivation as a relatively minor by-product the price is subject to wide fluctuation and substitutes of more stable price tend to be preferred by manufacturers.

Mannitol or **mannite,** $C_6H_8(OH)_6$, is a hexahydroxy alcohol extracted from manna. The sweetness is comparable to that of sugar. It is expensive and use is limited to replacement of sugar in diets for diabetics and to requirements as a laboratory reagent.

Sorbitol or **sorbit,** $C_6H_8(OH)_6$, is an hexahydroxy alcohol, very soluble in water or alcohol and isomeric with mannitol and dulcitol. It was originally obtained from the fruit of a mountain ash but is now produced by the electrolytic reduction of glucose in solution. While a crystalline substance, the commercial form is as a solution containing about 15 per cent of water. Quotations are on the basis of the anhydrous sorbitol present. It is used as a plasticizer to replace glycerine where the larger molecular weight offers technical or practical advantages.

Borneol, bornyl alcohol or **Borneo camphor,** $C_{10}H_{17}OH$, is soluble in alcohol or ether and slightly soluble in water. It is found in solid masses in a tree native to Sumatra and Borneo and also occurs mixed with an essential oil in an Asiatic woody herb. These two forms are optically active, the first being *dextro* and the second the *levo* form. Borneol is a secondary alcohol closely resembling camphor and can be obtained from it by reduction. The white translucent lumps have a camphor-like odor and are used in medicine, perfumery, in making celluloid, and for the synthetic production of camphor.

Linalool, $C_{10}H_{17}OH$, is an unsaturated tertiary alcohol found in a number of essential oils such as those from bois de rose, linaloa, lavender, coriander, and bergamot. It is a colorless liquid very slightly soluble in water but very soluble in alcohol and miscible with ether. Linalool has an odor similar to that of bergamot oil. It is used in lotions, hair preparations, soaps, etc., and in lily, lilac, jasmine, neroli, honeysuckle and gardenia perfume odors. **Nerol** is an isomeric alcohol used in orange-blossom and rose odors.

Geraniol, $C_{10}H_{17}OH$, is an unsaturated aliphatic alcohol of the terpene series obtained from oil of rose, geranium oil, palmarosa oil, lemon-grass oil, and citronella by forming the double compound with calcium chloride. It is isomeric with linalool, and is miscible with ether and soluble in alcohol. The pale yellow to colorless oil is sold in both imported and domestic grades. The imported is much more expensive. It has an odor resembling that of rose or geranium, and is used in low-price perfumes and as an odorant for soaps. Some grades contain nearly 90 per cent of alcohols, with some esters and aldehydes.

Eucalyptol, cineol or **cajeputol,** $C_{10}H_{17}OH$, is a colorless oil having an odor resembling that of camphor. It is very slightly soluble in water and soluble in alcohol, ether or oils. Eucalyptol is obtained by the fractional distillation of eucalyptus oil. The U.S.P. product is used in medicine. Lavender and pine odors often contain eucalyptol, and it is sometimes used as a flavor in dental preparations.

Terpine hydrate, $C_6H_8(OH)_2(CH_3)(C_3H_7)$, is a dipentene glycol, a colorless, crystalline compound formed by the slow reaction of dilute nitric acid, alcohol and oil of turpentine. A U.S.P. grade is sold, melting at 115-17° C. It is used for making terpineol and in medicine.

Terpineol or lilacine, $C_{10}H_{17}OH$, is a colorless liquid containing a mixture of isomeric compounds produced by reaction of terpine hydrate with phosphoric acid. It has a lilac odor and also occurs in a number of essential oils. Terpineol is slightly soluble in water but very soluble in alcohol or ether. A C.P. grade is sold for use in perfume. A crude grade known as *alpha*-**terpineol** or as a denaturing grade of terpineol, is much less expensive and is used for denaturing alcohol. It has been used for denaturing oils and fats for soap manufacture.

Menthol, $C_{10}H_{19}OH$, is a white crystalline alcohol soluble in alcohol, ether or chloroform. It is frozen out of peppermint oil and has the penetrating odor and cooling taste of peppermint. Synthetic menthol is derived from menthane. The U.S.P. grade of natural or synthetic menthol is quoted, melting at 41-3° C. A technical synthetic grade and a liquid quality are also available. Menthol is used in medicine, in confectionery, in perfumes and in cosmetics.

Citronellol, $C_{10}H_{19}OH$, is an unsaturated alcohol of the terpene series commonly obtained from oil of citronella but also present in other similar oils. The oily liquid is miscible with alcohol or ether. It is used in perfume for its sweet, rose-like odor. For the best results, freedom from geraniol is desirable.

Rhodinol or **reuniol,** is prepared by the fractional distillation of geranium oil and contains about 2 parts of citronellol and 1 part of geraniol. It is an oily liquid, nearly colorless, and solidifies on cooling. Uses are mainly in perfumes to replace oil of rose, and as an alcohol for rhodinol esters. Relatively inexpensive and very fine grades are available.

Furfuryl alcohol, $C_4H_3OCH_2OH$, is a colorless syrupy liquid which darkens on exposure to air and light. It is miscible with water and very soluble in alcohol or ether. This alcohol is obtained by the reduction of furfural, produced by the hydrolysis of oat hulls or corn cobs. The alcohol is a solvent in special lacquers and can be converted into resinoids. It is stated to react explosively with concentrated mineral acids.

Benzyl alcohol, $C_6H_5CH_2OH$, is a colorless liquid with a faintly aromatic odor, moderately soluble in water, very soluble in alcohol, and miscible with ether. It is the simplest alcohol of the aromatic series. Benzyl alcohol is prepared by the hydrolysis of benzyl chloride or benzyl acetate, or by simultaneous oxidation and reduction of benzaldehyde in the presence of alkali to benzyl alcohol and benzoic acid. Benzyl alcohol is expensive and use is limited to perfumes, flavors and synthetic purposes. It is a good solvent for musk and also serves as a fixative.

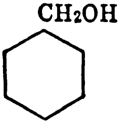
Phenyl ethyl alcohol, $C_6H_5C_2H_4OH$, is the next derivative to benzyl alcohol in the aromatic series of alcohols. It is a colorless, viscous liquid, slightly soluble in water and miscible with alcohol or ether. This alcohol has a faint rose odor and is produced synthetically for use in perfumes, particularly rose, lilac, neroli and jasmine. **Phenylpropyl alcohol** or **hydrocinnamic alcohol,** $C_6H_5C_3H_6OH$, is related in odor but tends toward lilac, hyacinth or wisteria.

Cinnamic alcohol, $C_6H_5CH{:}CHCH_2OH$, is a yellowish oil with a cinnamon odor tending toward hyacinth, miscible with alcohol, ether or chloroform. It is obtained from oil of cassia or oil of cinnamon, or is produced by distilling the product of the reaction between styracin and potassium hydroxide. Another grade is produced from storax in which it occurs naturally. It is used in flavors, as a fixative in hyacinth, lilac, lily, rose and similar perfumes and as a soap odorant.

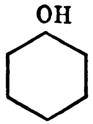
CHAPTER XX

PHENOLS AND THEIR DERIVATIVES

Alcohols are only one type of organic hydroxy compound. When a hydroxyl group is attached to an unsaturated ring-carbon of an aromatic compound the properties are radically changed and the compounds are called phenols. This is illustrated by benzyl alcohol as compared with the simplest of the phenols.



Benzyl alcohol



Phenol

Because of the use of phenols in disinfectants, several definitions need to be considered at this point. A **germicide** is anything which will destroy germs, and is usually applied to killing disease germs. In practice this means ordinary germs, particularly *Staphylococcus aureus* and *Eberthella typhi.* A germicide often is not effective against spore-forming bacteria such as those of anthrax or tetanus, which are particularly resistant. A **bactericide** is synonymous with a germicide, and either one is said to have **bactericidal properties.** An **antiseptic** prevents putrefaction or decay—prevents the growth of microorganisms but does not necessarily kill them. The term is usually applied to materials used on living tissue and they are said to be **bacteriostatic** in their properties. **Disinfectant** means ability to kill germs, to free from infection, and is substantially identical with germicide. To **sterilize** is a more modern term than to disinfect, and means to free from germs of all kinds. A **deodorant** has no direct relation to germs or bacteria, as it relates only to destroying or masking an odor. It may be indirectly related, as it may prevent putrefaction. An **insecticide** kills insects, generally specified types.

Phenols are acidic in nature. They dissolve in aqueous alkalies as alkali salts, which are not usually stable as solid compounds. They do not form the type of esters with acids that alcohols do. While they are hydroxy compounds they are sometimes incorrectly described as "oxy" compounds. This confusion arises from the German literature, where "oxy" is used for both O and OH radicals. Some names used here are chemically incorrect but necessarily retained because of wide commercial usage. Not all phenols are included in this chapter, as mixed compounds in which the other radical is of greater importance will be found elsewhere, for example, *para*-aminophenol is given with the amino compounds. Cresols are often present in commercial phenolic preparations, and are usually classed with phenol because of their similarity in properties. Other phenolic derivatives are often classed as phenols. The term is both general and specific.

Phenol or **carbolic acid,** C_6H_5OH, is a crystalline compound which is very soluble in cold water and miscible with hot water, alcohol or ether. In pure form it is white, but impurities usually color it pink to red. It is deliquescent and may take up enough water from the air to become liquefied. Phenol is obtained from the middle-oil fraction of coal tar by extraction with caustic soda, followed by neutralization with mineral acid or carbon dioxide, and distillation. Requirements have expanded in the past few decades so that such a supply is totally inadequate. A synthetic source is the sulfonation of benzene to form benzene sulfonic acid, followed by fusion with caustic soda. Reaction of chlorobenzene with caustic soda under pressure furnishes the major supply. The usual grade is U.S.P., which means not less than 98 per cent pure. U.S.P. liquefied phenol contains not less than 88 per cent of phenol and about 10 per cent of water. Phenol is a powerful antiseptic but is corrosive to tissue. This limits its antiseptic use largely to applications where it will not contact the skin in any substantial concentration. It is a major ingredient of the phenol-formaldehyde plastics, and is an important raw material for organic synthesis. It comes under the Caustic Poison Act, which is given in Appendix A.

Cyclohexanol or **hexalin,** $(CH_2)_5CHOH$, is a colorless, hygroscopic liquid having a camphor-like odor, prepared by reducing phenol with hydrogen in the presence of a catalyst. It is occasionally called **hexalene.** Its properties are closer to those of an alcohol than of a phenol. Hexalin is moderately soluble in water and soluble in alcohol or ether. It is used as a solvent for rubber, cellulose esters, phenols, etc., in products where a relatively expensive and nonvolatile solvent is suitable, and is also used as a solvent in detergents. The corresponding **methylcyclohexanol,** $H_3CCH(CH_2)_4CHOH$, is from reduction of a mixture of *o*- and *p*-cresols, and is similarly used where a higher-boiling solvent is desired.

Chlorophenol, ClC_6H_4OH, exists as three isomers of which two are important. *Ortho*-**chlorophenol** or *o*-**chlorophenol,** is a colorless to yellow or brown liquid having an unpleasant odor, soluble in water or alcohol. It is prepared along with the *para* isomer by direct chlorination of phenol or by treatment with sulfur oxychloride, SO_2Cl_2, and separated by fractional distillation. The *ortho* compound is an antiseptic but is mainly used as an intermediate in organic synthesis. *Para*-**chlorophenol** or *p*-**chlorophenol** is a white crystalline material having an unpleasant odor. It is extremely soluble in benzol, very soluble in alcohol and soluble in water. The *para* isomer is separated from the *ortho* isomer, or prepared from *para*-nitrophenol by replacement of the nitro group with chlorine. Its uses are similar to those of the *ortho* compound. *Meta*-**chlorophenol** cannot be prepared by direct chlorination and is unimportant.

Cresol or **methylphenol,** $CH_3C_6H_4OH$, may be any one of three isomeric compounds, or a mixture. The *meta* compound is a colorless liquid; the *ortho* and *para* compounds are crystalline. All are moderately soluble in water, miscible with alcohol or ether and have a phenolic odor. To meet U.S.P. requirements for cresol, not less than 90 per cent must distill between 195° and 205° C. This grade is sold. Mixed cresols, obtained in dark impure form from coal tar, are known as **cresylic acid.** *Ortho*-**cresol** is also prepared from *ortho*-chlorotoluene by autoclaving with caustic soda solution, a process similar to phenol manufacture. *Meta*-**cresol** and *para*-**cresol** are relatively of lesser importance. Cresylic acid is an important disinfectant but attacks the skin. Crude forms are used in cattle dips, so-called coal-tar disinfectants, etc. Better grades are present in products for use by humans. Cresol is used as a flotation reagent and in the manufacture of synthetic resins. *Ortho*-cresol is used in organic synthesis. This generic class includes **xylenols** or dimethyl phenols, $(CH_3)_2C_6H_4OH$, and various other homologous products. Xylenol is sold as high-boiling, low-boiling, imported pale 97-99 per cent and special resin grade.

Creosote is a crude phenolic mixture which may be from various sources. Pharmaceutically, the term refers only to that from wood tar. Industrially it is usually of coal-tar origin, distils at 200-300° and is often called **dead oil.** Uses are similar to those for low grade cresylic acid and one class blends into the other.

Coal-tar creosote is a yellow to brown mixture of phenolic substances with variable amounts of naphthalene present, in some grades sufficient to solidify the product at room temperature. Anthracene is sometimes present, either naturally or by addition of anthracene oil. The crude product is obtained by fractional distillation of coal tar, and usually contains 8-10 per cent of phenols. When distilled to separate naphthalene, as more fully described under coal tar, it gives tar-acid oils which are related, but higher in phenolic bodies. The coal-tar creosote classification is often much confused by the addition of related distillates from water-gas tar, blast-furnace tar, etc. Coal-tar creosote has a specific gravity heavier than water, should be liquid at 15° C. and is soluble in benzene and toluene. Grades offered are crude No. 1, crude No. 2 and refined. It is used as a source of naphthalene, for ore flotation, for timber impregnation to prevent rot and pests, and as an insecticide, germicide, etc. This is a source of phenolic materials of higher purity. Essentially it is an inexpensive mixture containing about 10 per cent of crude phenols. Coal-tar creosote in coal-tar solvent solution is also an article of commerce.

Low-temperature tar creosote is obtained from low-temperature coal distillation, but differs from coal-tar creosote in the presence of paraffin hydrocarbons, the absence of naphthalene, and a high tar-acid content. It has a specific gravity less than that of water. **Vertical-retort creosote** is quite similar but contains some naphthalene. **Producer-gas creosote** contains large amounts of high molecular-weight tar acids as well as paraffin hydrocarbons. **Water-gas tar creosote** is low in tar acids. **Blast-furnace tar creosote** is related to low-temperature tar creosote but contains much guaiacol and methyl guaiacol, and often 30-35 per cent of phenols. When fresh it can be refined to resemble wood-tar creosote.

Tar acids or **tar-acid oils** are dark liquids frequently almost black, fractions from coal-tar distillation. Their value depends on the content of cresols, etc. Frequently substantial amounts of anthracene and naphthalene are present. Usually as much phenol as conveniently possible has been removed. Tar acids are soluble in alcohol and coal-tar hydrocarbons. Grades are sold as containing the equivalent of 15 per cent and 25 per cent of phenol. Uses are in wood preservation and the manufacture of coal-tar type disinfectants. These oils are a relatively inexpensive form of crude phenolic compounds. They are also known as **dip oils** because of their use as insecticides for dipping cattle and sheep. This type of material is also known under the term of **sheep dip.**

Wood-tar creosote or **wood creosote** is an oily liquid having a burning, smoky taste, obtained by distillation of the tar derived from wood distillation, most commonly that of beechwood. That type may be sold as **beechwood creosote**, the grade called for in most pharmaceutical preparations. It is redistilled to remove the last traces of acetic acid. The creosote is then separated from hydrocarbons and basic materials such as pyridine, by extraction with an aqueous solution of sodium hydroxide, usually of about 10 per cent concentration. After separation from the insoluble portions, this is acidified, often with carbon dioxide, to liberate the purified mixture of phenolic bodies or wood-tar creosote. The finished material is a colorless to yellow or brown, refractive liquid heavier than water, distilling at about 205-225° C.—slightly soluble in water and miscible with alcohol, ether and many oils. Phenol esters as well as phenol and homologues are present. The major ingredients are guaiacol and methyl guaiacol. It is much less corrosive than pure phenol and is distinguished from coal-tar creosote by its solubility in glycerine. There is a U.S.P. grade defined as a mixture of phenols obtained from wood tar of which 90 per cent distils between 203 and 220° C. Grades quoted are U.S.P. hardwood and beechwood. It is used medicinally as an antiseptic by surface application, is the commercial source of guaiacol, and is used to make guaiacol carbonate and other derivatives. Because of its high price this product is not applicable for most industrial uses.

Creosote carbonate is a colorless to yellow oily liquid consisting of the carbonates of the compounds in wood creosote, largely cresol and guaiacol carbonates. It is prepared by treating a solution of creosote with caustic soda and carbonyl chloride. The U.S.P. grade has a specific gravity of not less than 1.145 at 25° C. and an ash content not over 0.1 per cent. It is used in medicine for the treatment of bronchitis and tuberculosis.

Pine tar is a viscid, dark brown liquid to semi-solid having a strong, characteristic odor, obtained by the destructive distillation of pine wood, that of *Pinus palustris,* or other species of *Pinus.* Its chief constituents are complex phenols. It is soluble in alcohol, ether or chloroform. A U.S.P. grade containing not more than 0.25 per cent of ash, is of minor importance as a treatment for skin diseases and bronchial disorders. Industrially in tonnage, it is used in ore flotation, roofing compositions, paints, plastics, tar soaps, asphaltic compositions, and as an impregnating medium for wood. The usual grade is retort tar.

Tar oil is the nearly colorless distillate from wood tar, which darkens with age. It contains substantial amounts of phenols and is soluble in ether or alcohol. Tar oil is used in insecticides and germicides and as a flotation oil. **Rectified tar oil** is a steam-distilled grade of the same material which, to be U.S.P. must be from pine tar.

Birch-tar oil or **oil of white birch** is obtained by the destructive distillation of the wood and bark of the birch tree, *Betula alba*. It is a dark, viscid liquid of characteristic odor. This crude material is often redistilled to produce a rectified grade somewhat lighter in color and of less intense odor. Both crude and rectified oils are quoted. The yellow liquid is poisonous as it contains phenols and cresols as well as other aromatic hydroxy compounds, turpentine, guaiacol, etc. It is used as a disinfectant and antiseptic, in dressing and preserving leather, and as a wood preservative.

Amber oil is, in the crude form, a dark brown to black viscous oil produced by the destructive distillation of amber. It has a strong characteristic odor. The major ingredients are terpenes and hydroxy compounds, but a small amount of fatty acid is present. By redistillation, a pale yellow to brown liquid is obtained. Both the crude and refined oil are soluble in ether or alcohol, and the refined moderately soluble in water. Both crude and refined grades are quoted, the latter being more than twice as expensive as the crude. Both are used in medicine as rubefacients, the refined being also an antispasmodic and stimulant.

Para-**tertiary amyl phenol,** $C_2H_5(CH_3)_2CC_6H_4OH$, is a white to pink or yellow crystalline compound, very soluble in alcohol or ether. It distils 95 per cent within 15° C., although this varies somewhat among different grades. It is a synthetic antiseptic agent and is used in the production of synthetic resinoids. *Ortho*-**amyl phenol,** an isomer, and **2,4-diamyl phenol** are also available. They are viscous yellow liquids similarly used.

Thymol, $(CH_3)_2CHC_6H_3(CH_3)OH$, is **2,5-methyl isopropyl phenol,** a white crystalline compound having a pleasant but strong and persistent odor. It is almost insoluble in water but exceedingly soluble in alcohol or ether. Thymol is isolated from horsemint oil or thyme oil by treatment with caustic soda, and separation and decomposition of the sodium salt with mineral acid. The odor resembles that of thyme. The U.S.P. grade melts between 48 and 51° C. Thymol is relatively expensive and is used as an antiseptic, vermifuge, preservative, and odorant, particularly in dental and hair preparations.

Thymol iodide, $(CH_3)_2CHC_6H_2ICH_3OH$, is a brown crystalline compound prepared by the reaction of thymol in alkaline solution with iodine in potassium iodide solution. The U.S.P. product contains not less than 43 per cent of iodine on a dry basis. It is insoluble in water but soluble in ether and very soluble in alcohol. Use is as an antiseptic.

Pyrocatechol or **pyrocatechin,** $C_6H_4(OH)_2$, is ***ortho*-dihydroxybenzene.** It is a colorless crystalline compound, very soluble in water, alcohol or ether. Pyrocatechol is prepared by heating guaiacol with hydriodic acid or by fusing phenolorthosulfonic acid with caustic potash at 350° C. It has a reducing action. The C.P. grade is available, also a very expensive resublimed product. It is used in photography, as an antiseptic, and in the synthesis of epinephrine.

Resorcinol or **resorcin,** $C_6H_4(OH)_2$, is ***meta*-dihydroxybenzene.** It is a colorless crystalline compound which turns pink on exposure to air. Resorcinol is extremely soluble in water or alcohol and very soluble in ether. It is prepared by fusing *meta*-benzenedisulfonic acid with caustic soda, and acidifying the dissolved melt with mineral acid. The material is not as strong a reducing agent as pyrocatechin, although isomeric with it. U.S.P., not less than 99.5 per cent pure, and technical grades are sold. It is used medicinally as an antiseptic and mild irritant, in textile dyeing and printing, and in organic synthesis, particularly for the preparation of fluorescein, phthalein and azo types of dyestuffs.

Eugenol, $C_6H_3OH(OCH_3)(CH_2CH{:}CH_2)$, is **4-allyl-2-methoxy phenol,** a colorless to pale yellow liquid very slightly soluble in water, very soluble in alcohol and miscible with ether. It has a clove odor and is obtained from oil of cloves by treating with an alkali, separating the alkali salt and liberating eugenol by the addition of acid. The U.S.P. grade distils between 250° and 255° C. It is used in medicine as a germicide, in flavors, in perfume, particularly for carnation odors, and for the preparation of isoeugenol which is used in making vanillin. **Isoeugenol** differs only in the group $-CH_2CH{:}CH_2$

being structurally rearranged to $-CH{:}CHCH_3$. This occurs on heating eugenol in alcoholic potassium hydroxide solution.

Guaiacol, $CH_3OC_6H_4OH$, is **pyrocatechol monomethyl ether,** which when pure is a white to yellowish crystalline solid melting at 28.5° C. It is soluble in water, miscible with alcohol or ether, and is obtained from beechwood creosote by extraction with alcoholic potash solution and washing with ether. The potassium compound is crystallized from alcohol, then decomposed with dilute mineral acid. It is also produced synthetically. Guaiacol usually is sold as a liquid because of small amounts of impurities which reduce the melting point. This darkens on exposure to air. U.S.P. solid guaiacol melts at about 28° C. U.S.P. liquid guaiacol distils 85 per cent between 200° and 210° C. Aside from medicinal uses it is oxidized to vanillin.

Guaiacol carbonate, $(C_7H_7O)_2CO_3$, is a white crystalline compound which is odorless, insoluble in water, but soluble in alcohol or ether. It is prepared by the reaction of sodium guaiacolate and carbonyl chloride, and is used in medicine in place of guaiacol or creosote.

Alpha-**naphthol** or α-**naphthol,** $C_{10}H_7OH$, is the simplest phenol derived from naphthalene. It is a colorless crystalline material with a phenolic odor, slightly soluble in water but very soluble in alcohol or ether. The product is prepared by fusing sodium *alpha*-naphthalenesulfonate with caustic soda and decomposing the product with hydrochloric acid. It is also present in coal tar fractions. *Alpha*-naphthol is used in organic synthesis, largely in the manufacture of dyes, and as an antiseptic.

Beta-**naphthol** or β-**naphthol,** $C_{10}H_7OH$, is a white crystalline compound which darkens on aging. It has similar solubilities to those of the *alpha* compound and is prepared by fusing sodium *beta*-naphthalene sulfonate with caustic soda and decomposing with hydrochloric acid. It is commercially more important than the *alpha* isomer, and sublimed and technical grades are sold. The U.S.P. grade melts between 120° and 122° C. It is used in organic synthesis, largely in the manufacture of dyes, and in medicine.

Hydroquinone, quinol or ***para*-hydroxybenzene,** $C_6H_4(OH)_2$, is a phenol, moderately soluble in water and very soluble in alcohol or ether. It is produced from quinone by reduction with sulfur dioxide. Medically it is an antiseptic and antipyretic. More important uses are as a photographic developer and as a reducing agent for special purposes.

Dimethyl hydroquinone, $C_6H_4(OCH_3)_2$, is a white crystalline derivative used in perfumes, particularly for soaps. The odor is persistent and resembles that of clover.

Phloroglucinol or **phloroglucin,** $C_6H_3(OH)_3,2H_2O$, is **1,3,5-trihydroxybenzene.** It is a white to yellow crystalline compound slightly soluble in water and very soluble in alcohol or ether. Phloroglucinol is prepared by fusion of resorcinol with caustic soda and decomposition of the melt with acid. C.P. and technical grades are sold largely for use in medicine.

CHAPTER XXI

ALDEHYDES AND KETONES AND THEIR DERIVATIVES

Aldehydes are characterized chemically by the way in which an oxygen atom is attached to carbon, that is, by the presence of the —CHO group joined to an organic radical. They are intermediate products between primary alcohols and their acids, and are therefore formed by the careful oxidation of primary alcohols. Aldehydes are very reactive and easily oxidized. The ending "al" is often used to indicate that a compound contains the characteristic aldehyde group, such as in acetal and citral

Formaldehyde or **formic aldehyde,** HCHO, is the simplest possible member of the aldehydes. Formaldehyde itself is a gas, but the common form of it is obtained on condensing the vapor and absorbing in water. A 37 per cent solution, called **formalin,** is prepared, and is the U.S P. standard. This solution is ordinarily meant when formaldehvde is mentioned or quoted The gas is also soluble in alcohol and ether. A small amount of methyl alcohol is present in the commercial product, including the U.S P grade, as well as polymerization products, since polymerization occurs very readily. It is produced commercially by the catalytic oxidation of methyl alcohol vapor by air when passed over heated copper or platinum gauze. Formaldehyde is a strong reducing agent. It is used in organic synthesis, particularly in the preparation of dyes of the triphenylmethane series such as rosaniline, and in hexamethylenetetramine, urea, paraformaldehyde, etc. Other uses are in embalming fluids, for the preservation of anatomical specimens, for hardening photographic film, and in other industries where the property of formaldehyde of hardening proteins and making them resistant to water, is of use. It is a major ingredient in the phenol-formaldehyde plastics, as well as a raw material at an earlier stage in urea plastics. It is an antiseptic and germicide.

Paraformaldehyde, $(HCHO)_n.H_2O$, is very soluble in water. It is a polymerization product of formaldehyde obtained by concentrating an aqueous solution of the latter *in vacuo,* or over concentrated sulfuric acid. The amorphous white solid has the odor of formaldehyde and changes back to formaldehyde on heating. It serves as a convenient source of formaldehyde for fumigant and disinfectant purposes, for waterproofing glues and for many other purposes.

Acetaldehyde or **acetic aldehyde,** CH_3CHO, boils at about room temperature. It is miscible with water, alcohol or ether and has a pungent suffocating odor. Acetaldehyde is formed from ethyl alcohol by passing the vapor over heated palladium black. It is also made synthetically from acetylene by causing the latter to unite with water. The gas is passed into a dilute solution of sulfuric acid containing mercuric oxide in suspension and the aldehyde is separated from unchanged acetylene by cooling. It is a powerful reducing agent and is often called **aldehyde.** The colorless liquid is used in organic synthesis, in disinfectants, in photography and in making synthetic rubber.

Aldol or **acetaldol,** $CH_3CH(OH)CH_2CHO$, is soluble in ether and miscible with water or alcohol. It is a polymerization product of acetaldehyde, in which two molecules of the latter have condensed to form the new compound. This condensation is brought about when acetaldehyde is treated with a dilute solution of an alkali, alkali cyanide, sodium sulfite or a mixture of sodium acetate with zinc chloride. A 95 per cent grade of the colorless or pale yellow viscous liquid is sold. It in turn polymerizes rather readily to form paraldehyde. Aldol is used in ore flotation, in engraving, and in organic synthesis such as in the manufacture of rubber accelerators.

Crotonaldehyde, $CH_3CH:CHCHO$, is a colorless liquid which darkens on exposure to air. It is moderately soluble in water, and miscible with alcohol, ether, benzol or petroleum hydrocarbons. It is formed on heating aldol with anhydrous sodium acetate. The liquid possesses a pungent suffocating odor. A technical grade is sold. It is used as an odorant agent in gases for the detection of leaks, since it is noticeable in very low concentrations, and in the synthesis of quinaldine and other synthetic organic chemicals.

Paraldehyde or **paracetaldehyde,** $(CH_3CHO)_3$, is a product of polymerization of acetaldehyde. It is a colorless liquid with a distinctive aromatic odor, soluble in water and miscible with alcohol, chloroform or ether. Paraldehyde is produced by polymerization of acetaldehyde with hydrochloric acid or zinc chloride. Structurally it is not an aldehyde but a cyclic ether. Technical and U.S.P. grades are available, the latter distilling between 120° and 125° C. Aside from medical purposes it is used for organic synthesis.

Acetal or **diethylaldehyde,** $CH_3CH(OC_2H_5)_2$, is a derivative of acetaldehyde formed by condensation of acetaldehyde with ethyl alcohol in the presence of acetic acid or a small amount of mineral acids such as hydrochloric or sulfuric. The colorless liquid has a pleasant characteristic odor and is very soluble in water, alcohol or ether. It is used medically, as an expensive solvent, and as an intermediate in the manufacture of synthetic jasmine.

Chloral hydrate, $CCl_3CH(OH)_2$, is not **chloral,** CCl_3CHO. Chloral hydrate is a hydrated aldehyde in colorless crystals of pungent odor and bitter taste. It volatilizes to a substantial degree on exposure to air. The solubility in water is extreme, that in alcohol or ether is great. Chloral is made by passing chlorine into absolute alcohol or aqueous acetaldehyde, chloral hydrate by addition of water to chloral. Chloral hydrate is used medicinally and in organic synthesis. It is the material used as **"knockout" drops.** The U.S.P. product is 99.5 per cent pure.

Butyraldehyde or **butyl aldehyde,** $CH_3(CH_2)_2CHO$, is miscible with water, alcohol or ether. It is obtained by the controlled oxidation of butyl alcohol by passing its vapors mixed with air over a suitable catalyst, and distilling off the aldehyde from unchanged butyl alcohol. It is also produced by the controlled oxidation of butyl alcohol with a mixture of chromic acid, sulfuric acid and water. The colorless liquid is used mainly in organic synthesis, as of rubber accelerators and synthetic resins.

Higher aldehydes are expensive odorants, usually derived synthetically from the related alcohols or acids. The terminology by the number of carbon atoms is used, paralleling that for the alcohols. **Heptylic aldehyde, heptyl aldehyde, oenanthic aldehyde, oenanthol** or **C-7 aldehyde,** $C_6H_{13}CHO$, is a colorless, refractive, oily liquid with an aromatic odor, soluble in alcohol and miscible with ether. It is derived from the vacuum distillation of castor oil. The fruity odor is heavy and leads to its use in bouquets. Some is used in organic synthesis. It is relatively inexpensive as compared with other perfume aldehydes. **Octylic aldehyde, octyl aldehyde, caprylic aldehyde** or **C-8 aldehyde,** $C_7H_{15}CHO$, is a colorless liquid obtained from the distillation of castor oil, soluble in alcohol or ether. It is used in jasmine and rose odors. **Nonylic aldehyde, nonyl aldehyde** or **C-9 aldehyde,** $C_8H_{17}CHO$, is a colorless liquid soluble in alcohol or ether and used for rose and tuberose odors. **Decylic aldehyde, decyl aldehyde** or **C-10 aldehyde,** $C_9H_{19}CHO$, is similar but tends toward a citrus type. It is used for rose, tuberose, and orange odors, and in colognes. **Undecylic aldehyde, undecyl aldehyde** or **C-11 aldehyde,** $C_{10}H_{21}CHO$, is a rose and lily type. **Lauric aldehyde, lauryl aldehyde** or **C-12 aldehyde,** $C_{11}H_{23}CHO$, has a citrus tone and is blended with other synthetics to give lift or tone to lily, violet and bouquets. **Methyl nonyl acetic aldehyde,** $C_9H_{19}(CH_3)CHCHO$, is sweet and is used to build up other aldehydes. Peach aldehyde is a lactone discussed under organic acids. **Strawberry aldehyde** or **C-16 aldehyde,** $C_{15}H_{31}CHO$, is used for the fruity odor and flavor. **Coconut aldehyde, cocoanut aldehyde** or **C-18 aldehyde,** $C_{17}H_{35}CHO$, is used in many odors such as gardenia, jasmine, etc.

Citronellal, $C_9H_{17}CHO$, is an unsaturated aldehyde found in lemon, lemongrass, citronella and similar essential oils. It is also obtained by the oxidation of citronellol. The liquid is very slightly soluble in water but miscible with alcohol or ether. It is used in inexpensive perfumes and in soaps. **Hydroxycitronellal,** $C_9H_{17}C(OH)_2$ is also quoted and is the product of reaction of the aldehyde with water. It is **citronellal hydrate,** a yellow oil soluble in alcohol or ether. It is also called **synthetic muguet** and is used as a perfume fixative and odorant, largely for violet tones in lilac, lily, jasmine and hyacinth. The dimethyl acetal is more expensive but sometimes is used to avoid skin irritation.

Citral, geranial or **geranialdehyde,** $(CH_3)_2C:CHCH_2CH_2C(CH_3):CHCHO$, is an unsaturated aldehyde found in the oils from lemon, geranium, orange-peel, lemongrass, bay leaves, etc. The light yellow liquid is insoluble in water but miscible with alcohol or ether. It is available in C.P. grade, and is used in flavors and in odors of the citrus or oriental types.

Furfural or **furfuraldehyde,** C_4H_3OCHO, is a colorless to reddish brown liquid, very soluble in water, alcohol or ether. It darkens on exposure to the air and is obtained from the pentoses of corn cobs, oat hulls, straw, jute, corn stalks, etc., by digesting these or similar products with moderately concentrated sulfuric acid. The term **furfurol,** which implies an alcohol structure, is also used for this aldehyde. Both refined and technical grades are sold. It is used in the manufacture of synthetic resins and molding compounds, disinfectants, deodorants, as a preservative of glue, in light-sensitive printing plates, as a nitrocellulose solvent and for the production of numerous chemical derivatives. It is the inexpensive starting material for derivatives of **furfurane,** C_4H_4O.

Benzaldehyde or **oil of bitter almonds,** C_6H_5CHO, is present in bitter almonds and the kernels of various fruits in the form of the glucoside, amygdalin. It is a colorless to yellow liquid having the odor of bitter almonds and is slightly soluble in water but miscible with alcohol or ether. Benzaldehyde is prepared from toluene by converting the latter to benzyl chloride by heating it with chlorine; benzyl chloride is in turn heated with lead nitrate, which converts it to benzaldehyde. The aldehyde may be made directly from toluene by direct oxidation with such metallic oxides as manganese dioxide or nickel peroxide, which gives a product free from chlorinated derivatives. Another method of manufacture is to heat benzal chloride with milk of lime, under pressure. When exposed to air, the aldehyde is oxidized to benzoic acid. Grades sold are technical, and should not be confused with U.S.P. oil of bitter almonds. It is used in the preparation of flavoring materials and odorants, and in the manufacture of dyes and of other synthetic organic compounds, including benzoic and cinnamic acids. The methyl derivative, **tolyl aldehyde,** $H_3CC_6H_4CHO$, is much less common. It is similar in properties, much more expensive, and used in flavors and perfumes because it is sweeter in tone.

Anisic aldehyde or **anisaldehyde,** $CH_3OC_6H_4CHO$, is obtained by the oxidation of anethole. The colorless liquid is slightly soluble in water but miscible with alcohol or ether. The hawthorn odor is blended with other odorants in perfumes.

Salicylic aldehyde or **salicyaldehyde,** HOC_6H_4CHO, is produced by heating phenol, chloroform and caustic potash together. The pale yellow liquid has a sweet odor and is used in small amounts in compounding perfumes. It has also been used as a disinfectant agent.

Cinnamic aldehyde, $C_6H_5CH:CHCHO$, occurs in the oils of cinnamon and cassia and in other essential oils, from which it may be obtained through the formation of its addition product with sodium bisulfite. It is prepared synthetically by the condensation of benzaldehyde with acetaldehyde in the presence of a dilute solution of caustic soda. The yellow oil is very slightly soluble in water but miscible with alcohol or ether. It has a cinnamon-like odor and is used in making extracts and perfumes.

Amyl cinnamic aldehyde, $C_5H_{11}C_6H_4CH:CHCHO$, is *alpha*-**amylcinnamic aldehyde,** a yellow oil with a modified cinnamon odor. The synthetic material is used as an odorant, largely in jasmine, lily and peach odors. The name **jasmine aldehyde** has been applied to it in the past. **Hexyl cinnamic aldehyde,** $C_6H_{13}C_6H_4CH:CHCHO$, is similar in odor and use.

Phenylacetaldehyde or **phenylacetic aldehyde,** $C_6H_5CH_2CHO$, is prepared by heating phenyl lactic acid with dilute sulfuric acid, or by the action of caustic soda on phenyl-*alpha*-chloroacetic acid. The colorless liquid is very slightly soluble in water but miscible with alcohol or ether. The odor is like that of hyacinth and it is used in perfume, particularly sweet pea, lily, jonquil, hyacinth, lilac and rose. It is sometimes sold in 50 per cent alcoholic solution to avoid polymerization.

Phenylpropylaldehyde or **hydrocinnamic aldehyde,** C_6H_5-C_2H_4CHO, is similar in properties to the acetaldehyde derivative but has a slightly different odor, tending toward the hyacinth.

Cumic aldehyde or **cuminic aldehyde,** $CH_3CHC_6H_4CHO$, is present in cumin oil and isolated from that source. The colorless to yellow liquid is soluble in alcohol or ether. It is an expensive odorant used in violet and related perfumes.

Heliotropin, piperonal or piperonyl aldehyde, $CH_2<O_2>$-C_6H_3CHO, is prepared by the oxidation of isosafrol or potassium piperate. The white crystals turn dark on exposure to light and are miscible with alcohol, ether or hot water. The compound is used in medicine, and in perfume as a fixative and for its heliotrope odor. In substantial amounts it tends to cause skin irritation.

Vanillin or **vanillic aldehyde,** $C_6H_3(OH)(OCH_3)CHO$, occurs as a natural efflorescence on vanilla beans, giving them their peculiar fragrance. It is prepared by oxidizing isoeugenol from oil of cloves, by oxidizing guaiacol, or by hydrolyzing coniferin, a glucoside found in the sapwood of fir trees, to give glucose and coniferyl alcohol. The latter is then oxidized to vanillin. Recovery from the lignin of the paper-pulp industry bids fair to dominate the market. The white crystalline powder is slightly soluble in cold water, moderately soluble in hot, and very soluble in alcohol or ether. It is sold as made from eugenol, from guaiacol, or from lignin for use as a synthetic vanilla flavor. It is an important perfume ingredient. Vanillin is the outstanding synthetic flavor in terms of the quantity used, which far exceeds 100 tons per year. This is partially due to the use of vanillin to round out other flavors, chocolate for example. **Ethylvanillin,** $C_6H_3(OC_2H_5)(OCH_3)$ CHO, is similar, but much more expensive and about three times as strong as vanillin. Several other vanillin esters are sold under trade names and have varying intensities of flavor and odor, all greater than that of vanillin.

Aldehol is not an individual chemical compound but is an oxidation product of kerosene which gives reactions of aldehydes. It has been used as a denaturant for ethyl alcohol, and as such has to meet definite specifications, including a specific gravity of not over 0.825, an approximate distillation range of 200-290° C. under fixed standard conditions, about 20 per cent solubility in ethyl alcohol and an iodine number of not less than 35. The denaturing grade is quoted.

Ketones are closely related to aldehydes. They can be considered as a substitution product of RCHO in which the H has been replaced with another radical to give RCOR. Thus ketones are characterized by the presence of a C:O group joined to two organic radicals. They resemble aldehydes in their chemical nature but are formed by the oxidation of secondary rather than of primary alcohols. The formation of both aldehydes and ketones is marked by the loss of two hydrogen atoms from the alcohol molecule. They are chemically quite active but not nearly so reactive as aldehydes. This reactivity is of the CO group which may be reduced to an alcohol, or oxidized with a break-up of the chain to give one or more organic acids. They form various addition products. The ending "one" is often used to indicate the ketone structure, as in acetone, anthraquinone, acetophenone, etc.

Acetone, CH_3COCH_3, is a colorless liquid miscible with alcohol, ether or water. Historically preparation is by dry distillation of commercial calcium acetate, which gives an impure product. This is further purified by isolation of the sodium-bisulfite addition compound, $(CH_3)_2CO,NaHSO_3$. This addition product is heated with a solution of sodium carbonate to liberate pure acetone. Water is removed by fractional distillation, the acetone dried over a desiccating agent and redistilled. This method is now obsolete. A more modern method of preparation is from isopropyl alcohol by passing the latter over heated metallic oxides which act as catalysts to oxidize it to form the ketone. Still another method of preparation is to ferment such starchy materials as corn or rice meal with

Bacillus butylicus at a slightly elevated temperature in the absence of air. Two volumes of butyl alcohol are formed to one volume of acetone. The C.P. grade is sold. Acetone is used as a solvent for lacquers, varnishes, fats, resins, in extraction of resins from rubber, as a solvent for cellulose acetate in the manufacture of acetate silk, as a solvent for cellulose nitrate in the manufacture of smokeless powders, in the manufacture of other chemicals such as chloroform, iodoform and sulfonal, in the synthetic manufacture of dyes and intermediates, as an absorbent for acetylene gas, and as a solvent in many other applications.

Methyl acetone is a mixture of acetone and other solvents of which a typical composition is 48 per cent acetone, 28 per cent of the 82 per cent grade of methyl acetate, and 24 per cent of methyl alcohol. It is sold as natural and synthetic. The latter commands a substantially higher price. The colorless liquid is anhydrous and is used as a solvent for gums, nitrocellulose, resins, etc., and as a varnish remover.

Methyl ethyl ketone or ethyl methyl ketone, $C_2H_5COCH_3$, is obtained by heating methyl acetoacetate with sulfuric acid, and distilling. It is very soluble in water and miscible with alcohol or ether. While slightly more expensive than acetone, it is similar in properties but less volatile. The colorless liquid is used in the production of synthetic organic chemicals and in general as a solvent.

Methyl propyl ketone or ethyl acetone, $C_3H_7COCH_3$, is another member of this series, prepared by distillation from a mixture of calcium acetate and calcium butyrate. It is colorless and miscible with alcohol or acetone but only slightly soluble in water. It dissolves in many organic solvents. Although substantially more expensive than acetone it is used as a higher-boiling solvent, particularly in lacquers.

Methyl butyl ketone or propyl acetone, $C_4H_9COCH_3$, is the next higher isomer. **Methyl isobutyl ketone,** $(CH_3)_2CHCH_2COCH_3$, is isomeric. They are colorless liquids soluble in ether, alcohol and many other organic solvents, prepared by methods similar to those for the simpler ketones. These ketones are mainly solvents for gums, resins and nitrocellulose in lacquers. **Methyl amyl ketone,** $C_5H_{11}COCH_3$, is similar in properties and uses.

Methyl hexyl ketone, $CH_3COC_6H_{13}$, is insoluble in water but miscible with alcohol or ether. It is a colorless liquid prepared by distillation of sodium ricinoleate with caustic soda. This classifies it as a remote derivative of castor oil. The odor is quite similar to that of apples. It is expensive and is used in the technical grade for organic synthesis, in perfumes and as an antiblushing agent in lacquers.

Methyl naphthyl ketone, $CH_3COC_{10}H_7$, is a white crystalline substance with an odor resembling that of orange blossoms. It is produced synthetically and used as an odorant and fixative, particularly in creams and soaps.

Mesityl oxide, $(CH_3)_2C{:}CHCOCH_3$, is **isopropylidene acetone.** It is produced by treatment of acetone with hydrogen chloride gas, and is a tonnage product. The colorless, oily liquid is soluble in water or ether and miscible with alcohol. It is a reagent in synthetic organic chemical manufacture.

Methylheptenone, $(CH_3)_2C{:}(CH_2)_2COCH_3$, is a colorless liquid, produced by controlled oxidation of the corresponding secondary alcohol, insoluble in water but miscible with alcohol or ether. It is used for organic synthesis.

Ionone or **violet ketone,** $C_{13}H_{20}O$, is a complex ketone which is the odorous material of violets and orris root. The faintly yellowish liquid is very slightly soluble in water, but miscible with alcohol or ether. **Pseudo ionone** is synthesized by condensing citral with acetone in the presence of alkaline earths and then boiling with a solution of sulfuric acid in glycerine to convert it to the product. Commercial grades usually contain around 90 per cent of ketone. By the use of methyl ethyl ketone the less common **methyl ionone,** $C_{14}H_{22}O$, is produced. Ionone is an important perfume ingredient in violet, rose, orris and bouquets. Much is used in soaps. The raspberry tone of its aroma renders it suitable for synthetic flavors, for which methyl ionone is even more satisfactory. Industrially, distinctions are made between *alpha*-ionone, *beta*-ionone, mixtures, ionone ketone, etc. Uses are similar.

Acetophenone, phenyl methyl ketone or **hypnone,** $C_6H_5COCH_3$, is prepared by condensing benzene and acetyl chloride in the presence of aluminum chloride or ferric chloride in carbon bisulfide. It is also formed by the distillation of a mixture of dry calcium acetate and calcium benzoate. The colorless crystals of acetophenone melt at about 19° C. so that the product is liquid at ordinary temperatures. Acetophenone is insoluble in water but miscible with alcohol or ether. It is used in new-mown hay, lilac and mimosa perfumery for its sweet orange-blossom odor, and as a sleep-inducing drug. It also is used for synthesis of more complex organic chemicals.

Methyl acetophenone or **methyl tolyl ketone,** $CH_3C_6H_4COCH_3$, is prepared from toluene by a method similar to that described for acetophenone. It is a colorless liquid soluble in alcohol, similar to acetophenone but less harsh, used as an odorant and in organic synthesis.

Benzylidene acetone, benzalacetone, methyl cinnamyl ketone or **methyl styryl ketone,** $C_6H_5CH:CHCOCH_3$, is prepared by treating benzaldehyde and acetone with a dilute solution of caustic soda. It is also obtained by distillation of the calculated proportions of calcium cinnamate and calcium acetate. The colorless crystals are purified by recrystallization. It is insoluble in water but very soluble in alcohol or ether. Use is in perfumery both as a fixative and for its odor, which resembles that of coumarin. It is particularly applicable to sweet pea, lavender and violet odors but must be used with caution as its odor is characteristic. It is also used in organic synthesis.

Carvone or **carvol,** $C_{10}H_{14}O$, is a ketone obtained by distillation from caraway, dill or spearmint oils. The colorless or slightly yellow liquid has an odor of caraway and is miscible with alcohol or ether, and very slightly soluble in water. It is used in perfumery, flavors, liqueurs and medicine.

Benzophenone or **diphenylketone,** $(C_6H_5)_2CO$, is a colorless, crystalline product, moderately soluble in alcohol or ether. It is produced by distillation of calcium benzoate, and used as an odorant and fixative in perfumes and soaps.

Anthraquinone, $C_6H_4(CO)_2C_6H_4$, may be considered as a double ketone, two phenyl groups joined by CO groups. The fact that they are in a ring structure alters the properties. Anthraquinone is prepared from anthracene by mixing a sludge of water and anthracene with sodium bichromate and caustic soda. After running through a mill the mixture is treated with sulfuric acid and steam, when the anthracene is oxidized to anthraquinone. The washed product contains about 95 per cent of anthraquinone, which can be further purified by sublimation. It is also produced by oxidation of anthracene in glacial acetic acid solution by chromic acid. A synthetic process of production is by heating phthalic anhydride with benzene in the presence of aluminum chloride. The addition compound is treated with a dehydrating agent to produce anthraquinone. The yellow needles are slightly soluble in alcohol, ether or benzene. It is sold as 99.5 per cent sublimed, and is used for the production of derivatives, mainly dyestuffs and intermediates such as alizarin and anthrapurpurin.

Methyl anthraquinone, $CH_3C_6H_3(CO)_2C_6H_4$, is obtained as white to yellow crystals by heating anthraquinone and methyl alcohol in the presence of sulfuric acid as a dehydrating agent. It is very slightly soluble in alcohol, soluble in ether and extremely soluble in benzene. It is used in the production of dyestuffs and intermediates.

Tetramethyldiaminobenzophenone or **Michler's ketone,** $[(CH_3)_2NC_6H_4]_2CO$, is made by heating dimethylaniline with phosgene, $COCl_2$, in an autoclave. The colorless to greenish crystals are purified by recrystallization. They are insoluble in water but very soluble in alcohol, ether or hot benzene. The ketone is an important intermediate in the manufacture of dyes.

Gum camphor is structurally a ketone, but is discussed with the natural gums because of the close relation of its use and because its physical properties are more important than the chemical properties.

CHAPTER XXII

ORGANIC ACIDS AND CLOSELY RELATED COMPOUNDS

Organic acids are usually weak or little ionized acids. By definition they give hydrogen ion in solution but the same deviations from this definition apply as have already been discussed in regard to inorganic acids. A few are quite strongly acid. Some are called **carboxylic acids** because of the characteristic acid group, –COOH, termed a **carboxyl group.** They may be monobasic or polybasic, examples being formic, acetic and butyric, containing one carboxyl group, oxalic and maleic acids containing two carboxyl groups and citric containing three. The organic radical may be straight-chain or cyclic, as in propionic and benzoic acids, respectively.

Sulfonic acids are organic acids containing an SO_2OH group joined to an organic radical through the sulfur atom. They differ from organic sulfates in that the latter are linked to other radicals by means of an oxygen atom. A simple example of a sulfonic acid is sulfanilic acid. In general, sulfonic acids are stronger acids than carboxylic acids, although the other radicals and groups present greatly affect the chemical nature and reactivity of the individual compounds. Organic sulfates, also included here, are both esters and acids, being esters of an alcohol with sulfuric acid but leaving one replaceable hydrogen, $ROSO_3H$. Organic acids form salts, the hydrogen of the carboxyl, sulfonic or sulfate group being replaced by metallic ion. Organic acids should not be confused with phenols, which are hydroxyl derivatives of cyclic hydrocarbons having acidic properties, but differing in structure and in other characteristics. Thus carbolic acid and cresylic acids are chemically phenols, not organic acids. Similarly many other compounds called acids will not be found in this chapter but in that on phenols. Some acid derivatives such as acid chlorides and acid anhydrides are included here because of close relationship to organic acids.

Formic acid, $HCOOH$, is the simplest and strongest of the series of aliphatic monobasic acids. It is a colorless liquid with a pungent odor, miscible with water, alcohol or ether. It occurs in some mineral waters, in muscle, and in animal secretions such as the stings of insects. In some reactions it behaves like a reducing agent, as in the reduction of silver salts. Methods of production are by the oxidation of methyl alcohol or of formaldehyde, or by heating oxalic acid with glycerine at 100-110° C. In concentrated form, it is prepared by dissolving sodium formate in 90 per cent formic acid and then distilling with concentrated sulfuric acid. C.P. formic acid is sold at 90 per cent concentration, and technical grades are sold varying in concentration from 75 to 90 per cent. It is used in electroplating, in dyeing and processing textiles, in the production of formates and esters including cellulose esters, and for numerous other purposes.

Acetic acid or **vinegar acid,** CH_3COOH, is a colorless liquid characterized by the sharp taste of vinegar. It is the second of the series of aliphatic acids and the most widely used organic acid. Because the anhydrous acid solidifies at 16.6° C. it is called **glacial acetic acid** to distinguish it from diluted forms. It mixes with water, alcohol or ether. Impure acetic acid in dilute form is obtained by the fermentation of dilute alcoholic liquors such as "hard" apple cider or wines. Unless qualified, **vinegar** means a solution of not less than 4 per cent of acetic acid obtained by fermentation of apple cider, by ruling of the Food and Drug Administration. Vinegars from other sources are described by suitable adjectives such as **wine vinegar, beet root vinegar, tarragon vinegar,** etc., often having characteristic flavors. **Malt vinegar** is colorless and is obtained by trickling alcohol from malt over beech shavings. This is known as the **quick vinegar process** which is also applied to alcohol from any source in producing **spirit vinegar. Double vinegar** is a vinegar of double strength.

A more concentrated acetic acid may be obtained from vinegar by neutralizing with lime, isolating the resulting calcium acetate, mixing this with sulfuric acid, and distilling the volatile acetic acid. A substantial but declining proportion of commercial acetic acid is obtained from the destructive distillation of wood. The acidic product is neutralized with lime, and acetic acid recovered from the calcium acetate by distillation with sulfuric acid. A method of production of increasing importance is by synthesis, as follows: Limestone and coal react in the electric furnace to form calcium carbide. Acetylene is produced from this by the addition of water. The acetylene may be converted into acetaldehyde by passing into hot dilute sulfuric acid containing mercuric sulfate, which acts as a catalyst. Acetaldehyde is oxidized to acetic acid by air or oxygen in the presence of a catalyst consisting of a metallic oxide. Both natural and synthetic grades of glacial acetic acid are quoted. The U.S.P. standard for acetic acid calls for 36-37 per cent of acetic acid, for 5.7-6.3 per cent in dilute acetic acid, and for 99 per cent in glacial acetic acid. Commercial or redistilled grades are sold at 28 per cent, 50 per cent, 70 per cent, and 80 per cent. Pure acetic acid is quoted at 30, 36, 60 and 80 per cent. To compare the relative cost in any given quotation in terms of anhydrous acid, multiply the price per pound by the corresponding factor given in the following table:

Per Cent Acetic Acid	Sp. G.	Factor to Calculate Price to That for Anhydrous Acid
4	1.0052	25.00
28	1.0388	3.57
30	1.0412	3.33
36	1.0481	2.78
50	1.0615	2.00
60	1.0685	1.67
70	1.0733	1.43
80	1.0748	1.25

Acetic acid is covered by the Caustic Poison Act, given in Appendix A.

Acetic acid is very commonly used when an organic acid is desired and a liquid acid is permissible. As a solvent it enters into many synthetic organic processes, and it is also used as a reacting chemical in organic synthesis. Many acetates are produced from it by neutralization. Esterified with cellulose, the important cellulose acetate is obtained. These are only indicative of the multitude of uses which extend into dyeing, pharmaceutical manufacture, etc.

Pyroligneous acid is a crude, yellow to red liquid which is a mixture of materials from wood distillation. The crude product contains methanol, acetic acid, acetone, furfural and various tars. It is used for the manufacture of acetic acid and acetone as well as for the separation of various other constituents, but is steadily declining in importance.

Acetyl chloride, CH_3COCl, is a colorless to light yellow liquid with a strong odor, giving off very irritant fumes. It is produced by the reaction of glacial acetic acid with phosphorus trichloride. The liquid reacts violently with water or alcohol to liberate hydrogen chloride and form acetic acid or ethyl acetate respectively. It is miscible with the majority of anhydrous organic solvents. Uses are in organic synthesis such as in the preparation of acetic anhydride, intermediates, dyes, and pharmaceuticals.

Acetic anhydride, $(CH_3CO)_2O$, is the material which, mixed with water, will form acetic acid. It is more expensive than the latter, so naturally acetic acid is not made in that way. Distillation of sodium acetate with acetyl chloride gives the anhydride but the lowest-cost process is probably by the reaction of acetic acid with ketene, $H_2C:CO$, a very simple synthesis. Acetic anhydride is miscible with many anhydrous solvents such as alcohol or ether. It is an important synthetic organic chemical reagent, as in the manufacture of cellulose acetate.

Monochloroacetic acid, chloroacetic acid or **chloracetic acid,** $CH_2ClCOOH$, is the monochloro-derivative of acetic acid. Introduction of the chlorine atom increases its activity as an acid. It forms colorless, deliquescent crystals, extremely soluble in water and soluble in alcohol or ether. Chloroacetic acid is prepared by passing chlorine into a boiling mixture of 1 part of sulfur and 10 parts of acetic acid. It is very corrosive to the skin. The 99 per cent and technical grades are used largely for the synthesis of dyestuffs such as indigo, and as a reagent in varied organic reactions. It is relatively inexpensive.

Trichloroacetic acid or **trichloracetic acid,** CCl_3COOH, is a fairly strong acid, being made notably stronger than acetic acid by the addition of the chlorine atoms. It forms colorless, deliquescent crystals having a slight characteristic odor. Trichloroacetic acid is extremely soluble in water and dissolves readily in alcohol or ether. It is prepared by oxidizing chloral hydrate with fuming nitric acid, or from glacial acetic acid by its reaction with chlorine in the presence of a suitable catalyst. The U.S.P. grade is 99 per cent pure. Use is limited because it is expensive. The acid attacks the skin readily and in this connection finds some medicinal use.

Lactic acid, ***alpha*-hydroxypropionic acid** or **α-hydroxypropionic acid,** $CH_3CHOHCOOH$, is a colorless to brown viscous liquid. It is miscible with water, alcohol or ether. The acid is present in sour milk due to the bacterial fermentation of milk sugar, lactose. Other sugars and starch can also be fermented to give this acid by inoculation with any of several varieties of lactic-acid forming bacilli. In practice it is obtained by fermenting milk, solutions of starch, or grape sugar, or a mash of corn or potatoes. As soon as it is formed, the acid is neutralized with calcium carbonate or zinc carbonate. The solution of the lactate is concentrated, the acid liberated with sulfuric acid and the lactic acid distilled. Sulfuric acid is sometimes present as an impurity in commercial lactic acid. U.S.P. 75 per cent and 85 per cent grades are quoted but the present U.S.P. grade is equivalent to 85 to 90 per cent. It contains a mixture of the acid and the anhydride. Light grades are quoted as 22 per cent, 44 per cent, 50 per cent edible grade and 50 per cent plastic grade. The plastic grade is more expensive than the edible grade. Technical dark grades are quoted at 22 per cent and 44 per cent concentration. It is used as an organic acid less volatile than acetic. Applications of the edible grades are in the manufacture of cheese, sauerkraut, pickles, extracts, confectionery and beer, and in medicine. Technical grades are used, aside from in plastics, in dyeing and textile printing, as a dye solvent such as for induline, nigrosine, and spirit-blue, in tanning for deliming of hides, etc.

Propionic acid or **methylacetic acid,** CH_3CH_2COOH, is a liquid belonging to the lower range of the aliphatic series of acids. It is colorless, has a pungent odor, and is miscible with water, alcohol or ether. The acid is obtained from beetroot molasses and purified by distillation, or produced by oxidation of normal propyl alcohol with chromic acid. The refined grade is used in the manufacture of perfume esters and artificial fruit flavors. A technical grade is also sold for similar purposes and for use in solutions for electroplating nickel.

Butyric acid or **ethylacetic acid,** $CH_3(CH_2)_2COOH$, occurs as the glyceride in a few fats. Together with free caproic acid it produces the odor characteristic of rancid butter. Butyric acid is classed as the lowest molecular-weight fatty acid. It is a colorless oily liquid, moderately soluble in water and miscible with alcohol or ether. It is formed by butyric fermentation of sugars, fats and other substances, such as the fermentation of molasses residues or of starch paste. Commercial grades are 90 per cent and 95 per cent edible, and 99 per cent synthetic acid. Since the calcium salt is soluble the acid is used as a deliming agent. Many of its synthetic esters are important as perfuming or flavoring ingredients. The free acid is also used in minor amounts in this way. For synthetic purposes, in some cases **butyric anhydride,** $(CH_3(CH_2)_2CO)_2O$, is preferred.

Crotonic acid, $CH_3CH:CHCOOH$, occurs in croton oil and is characterized by the presence of one double bond. Its colorless crystals are moderately soluble in water and soluble in alcohol, ether or petroleum ether. The acid is recovered from crude wood distillate or is prepared by heating malonic acid with paraldehyde and glacial acetic acid. Another synthesis is by the reduction of **acetoacetic acid,** CH_3COCH_2COOH, with sodium amalgam. It is a relatively expensive material, used in organic synthesis and for the stabilization of solutions of driers for protective coatings.

Caproic acid or **capronic acid,** $C_5H_{11}COOH$, occurs as the glyceride in butter and coconut oil. Being higher in the homologous series than butyric acid, it is almost insoluble in water. It is soluble in alcohol or ether and is obtained by fractional distillation from crude butyric acid. This acid can also be produced by the proper fermentation of cheese. The odor resembles that of perspiration. It is an expensive ingredient in organic synthesis, largely for the manufacture of esters.

Capric acid, $CH_3(CH_2)_8COOH$, is recovered from coconut-oil fatty acids. It is almost insoluble in water but soluble in alcohol or ether, and has an unpleasant odor. Use is for the esterification of alcohols, the resulting esters being used in flavors or perfumes.

Myristic acid, $CH_3(CH_2)_{12}COOH$, is a white crystalline acid, very soluble in alcohol or ether. It may be obtained from coconut-oil fatty acids by fractionation, this method displacing that of recovery from saponified oil of nutmeg. The acid is available in technical and white redistilled grades, for use in the synthesis of esters for flavors and perfumes, in cosmetics and for making special soaps.

Gluconic acid or **glyconic acid,** $CH_2OH(CHOH)_4COOH$, is a sirupy, odorless liquid obtained by the oxidation of glucose or cane sugar with chlorine or bromine. It may be largely present as an isomer, lactone. The acid is miscible with water and is sold in 50 per cent solution for use in tanning, in metal cleaning and in medicine.

Abietic acid, $C_{19}H_{29}COOH$, is a yellow powder, very soluble in alcohol or ether, obtained by liberation of the acid from rosin soap or digestion of rosin with alcohol. It is closely related to the fatty acids and its soaps are used in admixture with those of fatty acids. The acid is used in the production of driers for use in protective coatings. Rosin is largely abietic acid but is discussed as a natural resin because of its major use in the resin field.

Tall oil or **tallol** is a term for a fatty acid from pine wood. When the wood chips are pulped, the fatty acids are liberated and combine with alkali in the digester as soaps. When separated from the cellulose they are liberated with acid and purified to a greater or lesser extent. Contrary to what might be expected, the acids are not mainly abietic but consist of substantial amounts of various acids of the fatty series, with sterols, higher alcohols and other unsaponifiable matter. Proportions vary with source and the degree of purification. Rosin acids vary from 10-60 per cent, nonacid ingredients from 5-20 per cent, and fatty acids make up the balance. Constants cannot be given because of the wide variation in composition. The color is light yellow to almost black. Uses are for replacement of fats and fatty acids in soaps, for emulsions, for sulfonation, when esterified, as a paint oil, etc. The production is increasing rapidly as the United States turns to southern woods for pulp supplies, and may exceed 50,000 tons annually within a few years.

Rosin oil is a colorless to brown, odorless, viscous liquid obtained as the first fraction boiling above 360° C., in the distillation of rosin. It contains substantial amounts of free abietic acid and is soluble in oils, chloroform or ether. Rosin oil is purified by redistillation and quoted as first, second and third rectification. Medically it is an antiseptic. Industrially it is a non-drying adhesive, a solvent for many complex materials such as are used in greases, and is used in inks, varnishes, etc.

Fatty acids, as the term is used industrially rather than scientifically, consist of stearic, oleic and palmitic acids primarily, with several of lesser importance. Solubility in water decreases with an increase in the length of the carbon chain, caprylic acid, $C_7H_{15}COOH$, being only slightly soluble and acids above it less so. The saturated acids above caprylic in the series are solids at ordinary temperatures, but even the C_{17} unsaturated acids are liquid. These acids are distributed widely in nature, largely in the form of glyceryl esters. They are obtained from the esters known as saponifiable fats or oils, by hydrolyzing or saponifying according to various methods. One may be by reaction with alkali to form soap and glycerine; after removal of the glycerine the fatty acid is liberated from the soap with an inexpensive mineral acid. This is theoretical rather than practical. A commercial method of production is to hydrolyze the fat with live steam in the presence of a very dilute mineral acid and a suitable emulsifying agent, which aids in breaking up the fat or oil into small droplets. An aromatic sulfonic acid so used is known as the **Twitchell reagent** and the process as the **Twitchell process.** The fatty acids thus liberated are distilled.

Fatty acids are often sold in mixed form according to the oil from which they are derived, such as linseed-oil fatty acids, coconut-oil fatty acids, etc. Aside from use in the production of heavy metal salts they are used directly in making soap, there being a fine economic balance between producing fatty acids and glycerine, then making soap from the fatty acids, and making soap by saponification with alkali and separating the glycerine from the soap.

Stearic acid, $CH_3\ (CH_2)_{16}COOH$, is a white to light yellow saturated straight-chain fatty acid. As the glyceride it occurs in association with oleic acid in most animal and many vegetable fats and oils. Beef fat is high in stearic acid. Fatty acids with this length of carbon chain are insoluble in water but moderately soluble in alcohol or ether. Stearic acid is obtained by the hydrolysis of natural fats. Saponification and distillation types are quoted, the former at a slight premium. Of the three subgrades, single-pressed, double-pressed and triple-pressed, the single-pressed contains the most admixed oleic acid, the triple-pressed the least. While usually sold in cake form, some is powdered for sale at a small premium. Stearic acid, the fatty acid, is not to be confused with stearin, the glycerine ester of stearic acid. Stearic acid is widely used in cosmetics, and in candles to harden them. It has many varied minor applications which may depend on its rather hard and slightly greasy nature rather than on its properties as an acid.

Oleic acid or **red oil,** $CH_3(CH_2)_7CH:CH(CH_2)_7COOH$, is obtained by the hydrolysis of natural fats high in olein. It is very soluble in alcohol or ether. Since natural fats are always mixtures, the oleic acid has to be separated from the solid fatty acids present. The fats are saponified and the free fatty acids allowed to settle in pans. Insoluble stearic and palmitic acids separate as solids, from which the liquid fatty acid is removed by means of filter presses. The product contains some linoleic and other fatty acids, and occasionally soap as impurities. Practically only about 94-7 per cent of fatty acid is usually present, the balance being hydrocarbons. Red oil is descriptive of the cheaper grades, which have a characteristic color and odor. When further refined the color can be reduced to a faint yellow and the objectionable odor removed. Special trade names are often assigned to grades. Red oil is used in varied special products. Often it is converted to soap during processing. It may even be used to make soap for sale as such, particularly textile soaps. Red oil is sulfonated and used in other ways in textile specialties.

Ricinoleic acid, $CH_3(CH_2)_5CH(OH)CH_2CH:CH(CH_2)_7$-$COOH$, occurs as the glyceride in castor oil. It is a light yellow liquid of characteristic odor and is miscible with alcohol or ether. It is characterized by the presence of one double bond and one hydroxyl group. The technical grade as sold is obtained by saponification of castor oil. Its main uses are in textile finishes and specialties.

Palmitic acid, $CH_3(CH_2)_{14}COOH$, is available in only small quantities under that name, but as distilled **palm oil fatty acid** is readily available. Other fatty acids are present but the major proportion is palmitic acid. The use is limited to compounding special soaps, greases, etc.

Linoleic acid, $CH_3(CH_2)_4CH:CHCH_2CH:CH(CH_2)_7$-$COOH$, is isolated from drying oils as a light yellow liquid. It is characterized by the presence of 2 double bonds. Linoleic acid is soluble in the common organic solvents and is used in the production of driers for protective coatings and emulsifying agents. **Linseed oil fatty acids** are an impure form of linoleic acid, also containing the other fatty acids of linseed oil. The product is available in dark, light and extra-white grades, and is used in the manufacture of driers for protective coatings.

Coconut oil fatty acids are derived from coconut oil and contain a large amount of **lauric acid,** $CH_3(CH_2)_{10}COOH$. They are available in a distilled grade and are used in producing soaps and emulsifying agents.

Mixed fatty acids are often quoted as **split oils,** and in general are the mixture of fatty acids liberated by hydrolysis of the respective oils. While the materials available as fatty acids vary from time to time with market conditions, mixed fatty acids from any saponifiable oil may appear under favorable market conditions. Among those not mentioned previously are fatty acids from hempseed oil, soybean oil, cottonseed oil, chinawood oil, perilla oil, sardine oil and sunflower seed oil. In most cases a white grade of fatty acids or split oil is available, with exceptions in the case of oils naturally quite dark. Further information about all these fatty acids and split oils can be obtained by reference to the composition of the oil itself. Such mixed fatty acids have many applications according to the oil from which derived; in producing emulsifying agents, varnish dryers, etc.

Oxalic acid, $(COOH)_2,2H_2O$, is sold in the form of colorless crystals which effloresce in dry air. It is the simplest dibasic organic acid. In the form of the acid potassium salt or the calcium salt it occurs in many plants. It is among the strongest of the organic acids, and is moderately soluble in cold water, extremely soluble in hot, and very soluble in alcohol or ether. Oxalic acid is produced from many organic oxygen-containing compounds by fusion with caustic alkali. Cellulose in the form of wood shavings or sawdust is the usual starting material. This is heated with a strong aqueous solution of potassium and sodium hydroxides at 240-250° C. Milk of lime is added to the solution of the salt formed, to precipitate calcium oxalate. The latter is treated with sulfuric acid, which precipitates calcium sulfate and liberates free oxalic acid. Calcium oxalate may be present as an impurity. It may also be produced by the oxidation of sugar with nitric acid. Oxalic acid is sold in large volume. It is used as a purifying agent in many processes such as in the manufacture of glycerine, as a precipitant for lime where its removal is desired, as a bleaching agent as in bleaching straw, or wood, to remove ink and rust spots because of its ability to form soluble iron compounds, as an ingredient of metal polish, largely as a salt, in printing and dyeing textiles, and for many analogous purposes. It is covered by the Caustic Poison Act, which is given in Appendix A.

Maleic acid or **maleinic acid** $(CHCOOH)_2$, is a dibasic acid which occurs as a colorless crystalline solid. It is extremely soluble in water, very soluble in alcohol and moderately soluble in ether. This acid is isomeric with fumaric acid and is obtained by the catalytic oxidation of benzene, from malic acid by distillation, or by heating the acetyl derivative of malic acid. A technical grade is sold for use in synthetic organic chemistry, and in textile dyeing and printing. **Maleic acid anhydride,** $(CHCO)_2O$, is also an article of commerce, a white crystalline material soluble in ether, acetone or petroleum ether, produced by dehydration of the acid and used in organic synthesis, and as a basis of resin manufacture.

Fumaric acid, $(CHCOOH)_2$, is a white, crystalline solid practically insoluble in cold water or ether but moderately soluble in hot water or alcohol. It occurs in several plants and fungi and is isomeric with maleic acid, the former being the *trans* form. the latter the *cis*. Fumaric acid is obtained by boiling monobromosuccinic acid with water, by heating malic acid alone to 150° C., or by heating it with hydrochloric acid, by heating maleic acid to 210° C., or by condensing malonic acid with glyoxylic acid in the presence of pyridine. It is much more expensive than the isomeric maleic acid and is used in organic synthesis and in mordanting textiles.

Malic acid, apple acid or **hydroxysuccinic acid,** $(COOH)\text{-}CH(OH)CH_2COOH$, is fairly widely distributed in nature, occurring in unripe apples, grapes, mountain-ash berries, cherries, gooseberries, currants, quinces and other fruits. It is a white crystalline compound extremely soluble in water and very soluble in alcohol or ether. This acid is obtained from unripe fruit, mountain-ash berries being most used, and chemically by the partial reduction of tartaric acid with hydriodic acid, or by the catalytic oxidation of benzene. When obtained from berries, these are pressed under water and the aqueous solution neutralized with lime. The calcium salt of malic acid is produced on evaporation. Treatment with sulfuric acid precipitates the calcium and liberates free malic acid. The technical grade is used in medicine, in the synthetic production of other chemicals and in food products.

Tartaric acid, dihydroxysuccinic acid or **dextro-tartaric acid,** $[CH(OH)COOH]_2$, is a colorless crystalline acid extremely soluble in water, moderately soluble in alcohol and slightly soluble in ether. It is widely distributed in nature, occurring abundantly in grapes. Tartaric acid is obtained in the form of acid potassium tartrate from the residues known as *argols* formed in wine vats during the fermentation of grape juice. It is separated as calcium tartrate and the salt decomposed with sulfuric acid. U.S.P. and technical grades are sold, both domestic and imported. The U.S.P. standard requires 99.5 per cent purity. It is used as the acid potassium salt in one form of baking powder, for the preparation of various tartrates, in tanning, in photography, in the textile industry, as a fruit acid in foods and beverages, and in various minor ways.

Seidlitz mixture or **Seidlitz powder** is an effervescent U.S.P. composition. The acid ingredient is tartaric acid, the alkaline ingredient a mixture of one part of sodium bicarbonate and three parts of sodium and potassium tartrate. These are used in the proportion of 2-2.4 grams of the acid ingredient and 9.5-10.5 grams of the alkaline salts, to be mixed just before adding water.

Citric acid or **hydroxytricarboxylic acid,** $C_3H_4(OH)(COOH)_3,H_2O$, may be in the form of colorless crystals or a white powder. It is extremely soluble in water or alcohol and moderately soluble in ether. The crystals effloresce in dry air and deliquesce in moist air. It is present in the juice of lemons, oranges, citrons, currants, gooseberries and other fruits and bulbs, and it is made on a large scale from lime or lemon juice. The juice is fermented for some time to free it from mucilaginous materials, then boiled, filtered and neutralized with calcium carbonate and milk of lime. The insoluble calcium citrate is decomposed with dilute sulfuric acid, filtered and evaporated to remove calcium sulfate. The crystals are finally obtained from the concentrated liquid. Tartaric acid may be present as an impurity, as this is also a naturally occurring acid in many of these fruits. Crystalline, granular and anhydrous forms may be obtained. The U.S.P. standard requires 99.5 per cent purity. Citric acid is used in flavoring extracts, confectionery, soft drinks, in medicine as a mild astringent, to produce effervescence with bicarbonates, for the preparation of citrates, in calico printing, and in electroplating.

Succinic acid or **ethylenedicarboxylic acid,** $(CH_2COOH)_2$, occurs in amber, in fossilized wood and in many plants. The colorless crystals are moderately soluble in cold water or alcohol, exceedingly soluble in hot water and slightly soluble in ether. The acid is obtained by the distillation of amber or by the fermentation of calcium malate or ammonium tartrate. Succinic acid is also produced synthetically by the reaction of dichloroethane and sodium cyanide, followed by hydrolysis and neutralization of the resulting succinic acid salt. It is used in organic synthesis and in medicine. On prolonged heating it forms **succinic acid anhydride,** $(CH_2CO)_2O$.

Adipic acid, $HOOC(CH_2)_4COOH$, is a white to yellow powder produced by the oxidation of fats and oils by nitric acid. It is slightly soluble in cold water and soluble in alcohol or hot water. Its use is in organic synthesis and in resin manufacture.

Sebacic acid or **1,8-octane-dicarboxylic acid,** $HOOCC_8H_{16}COOH$, is a colorless to yellow crystalline acid obtained by the dry distillation of castor oil with sodium hydroxide. It is almost insoluble in water but very soluble in alcohol or ether. Sebacic acid is used in the manufacture of plastics and candles, but mainly in the form of its esters in perfumes and flavors.

Benzoic acid, C_6H_5COOH, is the simplest acid of the aromatic series. It occurs in white crystals and is slightly soluble in cold water, moderately soluble in hot, and very soluble in alcohol or ether. The acid is usually prepared from toluene, which is chlorinated to form **benzotrichloride,** $C_6H_5CCl_3$, which in turn is heated with milk of lime to form calcium benzoate. The latter is decomposed with mineral acid to form free benzoic acid. It also occurs as a by-product in the conversion of toluene to benzaldehyde in the form of calcium benzoate, which is easily converted to benzoic acid. Toluene may be directly oxidized to benzoic acid by means of manganese persulfate and sulfuric acid, the benzoic acid being recovered by distillation with steam, but this is not a commercial process.

Benzoic acid occurs naturally in gum benzoin and as an ester in Peru and Tolu balsams. The U.S.P. grade must be 99.3 per cent pure. A technical grade is also sold. It is used for seasoning tobacco, for the manufacture of benzoates, as a mordant in calico printing, in organic synthesis, and as a preservative and antiseptic. When used in food products as the acid or as sodium benzoate, it must be declared on the label and must not exceed 0.1 per cent as sodium benzoate. Practically speaking it is the acid which is usually used as a food preservative but is only effective in most products in solutions of pH about 4.5-5.0. Many of its esters are used in flavors or perfumes.

Benzoyl chloride, C_6H_5COCl, is a colorless, pungent liquid decomposed by water or alcohol but miscible with anhydrous solvents. It is prepared by the action of phosphorus tri- or pentachloride on benzoic acid. The acid chloride is used as an intermediate in making organic compounds.

Benzoyl peroxide, $(C_6H_5CO)_2O_2$, is a white crystalline substance insoluble in water but soluble in alcohol, carbon bisulfide or oils. It is formed by the treatment of benzoyl chloride with barium peroxide. Aside from use in organic synthesis, it is a bleaching agent for oils, waxes, flour, etc.

Salicylic acid, *ortho*-hydroxybenzoic acid, or ***o*-hydroxybenzoic acid,** HOC_6H_4COOH, crystallizes in white needle-like crystals, almost insoluble in water but very soluble in alcohol or ether. It occurs in the leaves and stems of tulips and hyacinths, and as the methyl ester in oil of wintergreen. This acid is prepared from phenol, which is converted into the sodium salt and then heated under pressure with carbon dioxide. The sodium salt of salicylic acid thus obtained is dissolved in water, decolorized, acidified with mineral acid, and the free salicylic acid allowed to crystallize out. It is sold in a U.S.P. grade 99.5 per cent pure, and as technical. Major uses are in the manufacture of azo dyes and intermediates, drugs, and therapeutic agents. It has been widely used as a preservative in food, beer and wine, but its use in food has been forbidden in the United States, even if declared on the label. Salicylic acid is used as a preservative in many nonfood products.

Acetylsalicylic acid or **aspirin,** $CH_3CO_2C_6H_4COOH$, is a white crystalline powder obtained by the action of acetic anhydride on salicylic acid at an elevated temperature. Salicylic acid may be present as an impurity. It is slightly soluble in water but very soluble in alcohol or ether. The U.S.P. grade is sold at a purity of 99.5 per cent as a cure for headache. The term aspirin was formerly a trade name but is not now restricted.

Anthranilic acid, ***ortho*-aminobenzoic acid** or ***o*-aminobenzoic acid,** $H_2NC_6H_4COOH$, occurs as yellow crystals slightly soluble in water and very soluble in alcohol or ether. It is obtained by treating phthalimide with an alkaline hypobromite solution. Refined and technical grades are used in the manufacture of dyes, particularly indigo, and in the synthesis of perfumes and pharmaceuticals.

***Para*-aminobenzoic acid** or ***p*-aminobenzoic acid,** $H_2NC_6H_4$-$COOH$, is an isomer of anthranilic acid. It appears in the form of yellow to white crystals having solubilities similar to those of the *ortho* compound. This acid is obtained by the reduction of *para*-nitrobenzoic acid, or by oxidizing the acetyl derivative of *para*-toluidine and hydrolyzing the resulting acetamino acid. It is used in the synthesis of dyes and pharmaceuticals.

Phthalic acid or **benzenedicarboxylic acid,** $C_6H_4(COOH)_2$, is relatively unimportant but **phthalic anhydride,** $C_6H_4(CO)_2O$, is important. The anhydride occurs as large white needles, slightly soluble in hot water or ether but soluble in alcohol. It is prepared by the atmospheric oxidation of naphthalene at about 500° C. in the presence of vanadium oxide as a catalyst. Phthallic anhydride is used in synthetic organic chemistry for the manufacture of phthaleins such as phenolphthalein and dyes. It is a major ingredient of the phthalic anhydride resins, in which it reacts with glycerine.

Phenylacetic acid, ***alpha*-toluic acid** or **α-toluic acid,** $C_6H_5CH_2COOH$, is a white crystalline solid prepared by the alkaline hydrolysis of benzyl cyanide, which is formed by the action of potassium cyanide on benzyl chloride. This acid is moderately soluble in water but extremely soluble in alcohol or chloroform. It is an expensive ingredient in organic synthesis, and since it has a rose-like odor is used as an odorant and fixative in clover, neroli and jasmine perfumes, as well as in soaps.

Mandelic acid or **amygdalic acid,** $C_6H_5CH(OH)COOH$, is **phenylhydroxyacetic acid,** a white crystalline substance soluble in water, alcohol or ether. It is produced by the reaction of benzaldehyde with potassium cyanide in acid solution, followed by saponification of the nitrile produced. It is used in synthetic organic chemistry as an intermediate.

Cinnamic acid, ***beta*-phenylacrylic acid** or **β-phenylacrylic acid,** $C_6H_5CH:CHCOOH$, is a white crystalline solid very soluble in absolute alcohol or ether. It occurs naturally in Peru and Tolu balsams, and in storax. The product is commonly prepared by heating benzaldehyde, acetic anhydride and anhydrous sodium acetate to about 180° C., making the mixture alkaline with sodium carbonate, and removing excess benzaldehyde by a current of steam. The residual liquid is acidified with hydrochloric acid, which precipitates cinnamic acid. It is recrystallized from hot water. Other methods of preparation are by the reduction of phenyl propionic acid with zinc and acetic acid, by heating benzal malonic acid, or by condensing ethyl acetate with benzaldehyde in the presence of sodium ethylate. Refined cinnamic acid and its esters are used in the production of perfumes. The sodium salt and various esters are used therapeutically.

Sulfanilic acid, ***para*-aminobenzene sulfonic acid** or ***p*-aminobenzenesulfonic acid,** $H_2NC_6H_4SO_3H,2H_2O$, is prepared from aniline by heating it with concentrated or fuming sulfuric acid and pouring the cooled reaction product into cold water. The colorless efflorescent crystals are moderately soluble in water but very slightly soluble in alcohol or ether. Both C.P. and technical grades are available. It is used in organic synthesis as an important intermediate as in the production of quinone, dyes, etc. **Aniline disulfonic acid** or **aminobenzene disulfonic acid,** $H_2NC_6H_3(SO_3H)_2$, is the product of similar but more drastic treatment and is similarly used.

Metanilic acid, *meta*-**aminobenzene sulfonic acid** or *m*-**aminobenzene sulfonic acid,** $H_2NC_6H_4SO_3H,1\frac{1}{2}H_2O$, is isomeric with sulfanilic acid. It is much more expensive because produced by sulfonation of acetanilide and subsequent saponification of the acetamino group. The colorless crystals are soluble in water, alcohol or ether, and are used in organic synthesis.

Ortho-**toluene sulfonate** or **toluene** *ortho*-**sulfonic acid,** $CH_3C_6H_4SO_3H,2H_2O$, is a white crystalline compound, very slightly soluble in water and soluble in alcohol. It is a product of direct sulfonation of toluene and is used in synthetic organic chemistry, largely as a dye intermediate.

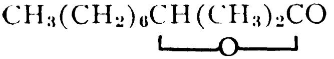
Para-**toluene sulfonechloride,** $CH_3C_6H_4SO_2Cl$, is a crystalline compound resulting from treating toluene with chlorosulfonic acid. It is a dyestuff intermediate.

Gallic acid, $C_6H_2(OH)_3COOH,H_2O$, is a colorless or slightly yellow crystalline solid moderately soluble in water or ether and very soluble in alcohol. It occurs in gallnuts, sumach, Chinese tea, pomegranate and root-bark. Chemically the structure is **3,4,5-trihydroxybenzoic acid.** A paste of powdered gallnuts and water is allowed to stand for several weeks, when the tannins present are slowly decomposed by the action of mold. Finally the paste is boiled with water and filtered. Crude gallic acid crystallizes out on cooling. N.F. VI and technical grades are sold. While a U.S.P. grade is occasionally quoted it refers to U.S.P. IX, now obsolete. It is used in the manufacture of several dyes such as anthracene brown and galloflavin, in writing ink, photography, paper manufacture, process engraving, as a special tanning agent and in pharmaceuticals.

Tannic acid, gallotannic acid, digallic acid, or **tannin,** occurs in gallnuts and the bark of various trees such as sumach, oak and hemlock, and in other plant products. There are varied structures and the formula, $C_{14}H_{10}O_9$, is only an average value. In the pure form it varies from light yellow to brown and is extremely soluble in water, alcohol or ether. It is a reducing agent and also a precipitant for many alkaloids and proteins. Its most characteristic property is the ability to form an insoluble compound with collagen, which constitutes the tanning of leather. Tannic acid is a strong astringent. It is obtained from gallnuts by extraction with alcohol and water, or alcohol, ether and water. Commercial grades are U.S.P., containing not over 12 per cent of moisture, and technical. It is used as a mordant in dyeing, as a constituent of inks, in the fining of wines, and in numerous other ways suggested by the above properties. Leather is tanned with tannic acid in cruder forms, such as sumac extract, quebracho extract, gambier extract, etc.

Camphoric acid, $C_8H_{14}(COOH)_2$, is obtained as colorless crystals by oxidizing camphor with nitric acid. It is slightly soluble in water but extremely soluble in alcohol or ether. This is a relatively expensive ingredient of pharmaceuticals.

Coumarin, $C_9H_6O_2$, is *ortho*-**hydroxycumaric anhydride,** the lactone of *ortho*-hydroxycumaric acid, a colorless crystalline compound, very soluble in chloroform and moderately soluble in alcohol. It has a fragrant odor like that of new-mown hay, and is isolated from Tonka beans or prepared synthetically by the reaction of salicylic aldehyde, sodium acetate and acetic anhydride. Another synthesis is by the chlorination of dicresyl carbonate and heating with acetate anhydride and anhydrous sodium acetate. It is used in perfumery, and in flavoring preparations of various types to give a vanilla-like taste. While but little less expensive than vanillin, it imparts about three times as much flavor per unit of weight. **Methyl coumarin,** $C_{10}H_8O_2$, is more powerful in odor and flavor value and more expensive.

Undecalactone or **peach aldehyde,** having the structure  $CH_3(CH_2)_6\underbrace{CH(CH_3)_2CO}_{O}$ is a lactone of an acid, rather than an aldehyde. It results from the destructive distillation of castor oil in the presence of superheated steam, followed by treatment of the resulting products with sulfuric acid to form the lactone. It is alcohol-soluble, and is used in peach and berry flavors, in jasmine-type perfumes, and in cosmetics for its peach odor.

Phenolphthalein, $(C_6H_4OH)_2COC_6H_4CO$, is a derivative of triphenylmethane, a cyclic acid anhydride, and is prepared by heating phthalic anhydride with phenol in the presence of a dehydrating agent. The compound is a white or light yellow solid, colorless in acid solution, but undergoing molecular rearrangement in alkaline solution to give a pink color. With a large excess of alkali it again becomes colorless. It is soluble in alcohol, ether or aqueous alkali, only slightly soluble in water. Yellow, and a U.S.P. grade, melting not below 258° C., are sold, the yellow being slightly cheaper. It is used in medicine as a laxative.

Santonin, $C_{15}H_{18}O_3$, is a white crystalline compound extracted from santonica, the unopened flowers of *Artemesia pauciflora.* It is the lactone of santoninic acid. The commercial forms are colorless plates or powder. Santonin is slightly soluble in water and very soluble in alcohol or ether. It darkens on exposure to light and is a U.S.P. preparation melting between 169° and 171° C. Its use is in medicine as an anthelmintic, tonic and emmenagogue.

Naphthenic acid, as sold, is not the **hexahydrobenzoic acid,** $C_6H_{11}COOH$, implied, but a complex mixture. The products are recovered from the petroleum industry, more particularly abroad, and sold in suspension or in solution in petroleum oil. The commercial forms are sold as sludges and in solutions with Saybolt viscosities of 240-280, 210-230 and 120-200. They are used, mainly as sodium salts, as emulsifying and wetting agents and for refining to form metal naphthenates. When sulfonated **sulfonaphthenic acids** are obtained, an equally crude mixture which is more soluble in water.

Furoic acid, pyromucic acid or **furane carboxylic acid,** C_4H_3OCOOH, occurs as white to yellow crystals, moderately soluble in water and very soluble in alcohol or ether. It is produced by oxidation of furfural with alkaline permanganate. One name developed from a method of production, which was by heating mucic acid to 180° C. It is used for further steps in organic synthesis, and in the preparation of bactericides and fungicides.

A series of complex **naphthalene sulfonates** are used as dye intermediates. They are largely known by special names rather than by their structural names. The processes of manufacture are usually complex, involving differences in degree of sulfonation, etc. **Neville and Winther's acid** is **1-naphthol-4-sulfonic acid** or *alpha*-**naphtholsulfonic acid**, $HOC_{10}H_6SO_3H$. **Peri acid** or **naphthionic acid** is **1-naphthylamine-8-sulfonic acid**, $H_2NC_{10}H_6SO_3H$. **Cleve's acid** is a mixture of **1-naphthylamine-6-sulfonic acid** and **1-naphthylamine-7-sulfonic acid**, $H_2NC_{10}H_6SO_3H$. **Epsilon acid** is **1-naphthylamine-3,8-disulfonic acid**, $H_2NC_{10}H_5(SO_3H)_2$. **Schoelkopf's acid** is **1-naphthylamine-4,8-disulfonic acid**, $H_2NC_{10}H_5(SO_3H)_2$. **Koch's acid** is **1-naphthylamine-3,6,8-trisulfonic acid**, $H_2NC_{10}H_4(SO_3H)_3$. **1,2,4 acid** is **1-amino-2-naphthol-4-sulfonic acid**, $H_2NC_{10}H_5(OH)SO_3H$. **S acid** is **1-amino-8-naphthol-4-sulfonic acid**, $NH_2C_{10}H_5(OH)SO_3H$. **H acid** is **1-amino-8-naphthol-3,6-disulfonic acid**, $H_2NC_{10}H_4(OH)$-$(SO_3H)_2$. **Chicago acid** or **SS acid** is **1-amino-2-naphthol-2,4-disulfonic acid**, $H_2NC_{10}H_4(OH)(SO_3H)_2$. **Laurent's acid** is **1-nitronaphthalene-5-sulfonic acid**, $O_2NC_{10}H_6SO_3H$. **Tobias' acid** is **2-naphthylamine-1-sulfonic acid**, $H_2NC_{10}H_6SO_3H$. **Broenner's acid** is **2-naphthylamine-6-sulfonic acid**, $H_2NC_{10}H_6SO_3H$. **Monosulfonic acid, Cassella's acid** or **F acid** is **2-naphthylamine-7-sulfonic acid**, $H_2NC_{10}H_6SO_3H$. **J acid** is **2-amino-5-naphthol-7-sulfonic acid**, $H_2NC_{10}H_5(OH)SO_3H$. **Gamma acid** is **2-amino-8-naphthol-6-sulfonic acid**, $H_2NC_{10}H_5(OH)SO_3H$. **2 R acid** is **2-amino-8-naphthol-3,6-disulfonic acid** $H_2NC_6H_4(OH)(SO_3H)_2$. All are dyestuff intermediates.

Ascorbic acid or **cevitamic acid**, $C_6H_8O_6$, is **vitamin C**, the first vitamin identified as to structure. It was formerly called **hexuronic acid**, but the implied structure is incorrect. Strictly speaking, it is not structurally an organic acid but has acidic properties. It is isolated from citrus fruit juices and also produced synthetically by the controlled oxidation of dextrose. Ascorbic acid is very expensive, and only used medically.

Ichthyol consists of the ammonium salt of a sulfonated hydrocarbon of mineral origin. Ichthyol is soluble in water or light petroleum hydrocarbons and partially soluble in alcohol or ether. It is manufactured from the distillate of bituminous shales found in Seefeld, Tyrol, and is a dark liquid with an odor related to that of crude oil. It is used medically as an antiphlogistic and antiseptic. Use is largely external.

Sulfonated oils are a form of processed oils. The term is incorrect since the oils are sulfated and contain the $-OSO_2OH$ group, not the $-SO_2OH$ group bound directly to carbon. The trade term of sulfonated oil may be expected to persist. The general process of so-called **sulfonation** is by agitation with sulfuric acid, which adds at an unsaturated linkage, or in the case of castor oil by reaction with the hydroxyl group of the ricinoleic acid ester. The temperature is carefully controlled during this operation. An alternative process makes use of sulfonyl chloride. After sulfonation, excess sulfuric acid is neutralized in whole or in part, and the oil washed with sodium sulfate solution, in which the oil is substantially insoluble.

Sulfonated oils are soluble in water, some giving a clear solution, others a cloudy dispersion. Trade requirements for special purposes depend on the stability to acid and other special properties. The sulfonated oils of commerce always contain water, sodium sulfate, free fatty acid, or the soap produced from it by neutralization, and unsulfonated raw material, as well as the fatty glyceride sulfate (sulfonate). Sulfonated fatty acids are also available although not commonly quoted. Grades of sulfonated oils are significant only as indicating the fat content and total sulfonated materials. The same grade differs from batch to batch, so that reliable standardization is only approximated at best by the manufacturer's blending of several batches. The quoted grades are very numerous, those which follow being only representative. Uses of sulfonated oils are as wetting agents, detergents, assistants in dyeing, emulsifying agents, softening agents on textiles or leather, etc. Varied grades are preferred by different industries and even by different plants in the same industry often without adequate technical reason.

Sulfonated castor oil is the most common sulfonated oil. It is still called **Turkey-red oil** because of its use in dyeing with alizarin. Commercial grades are 50 per cent (48 per cent fat), 75 per cent (63 per cent fat), and 80 per cent (68 per cent fat). The first is but slightly sulfonated, the latter two more highly sulfonated. Sometimes grades are referred to as single sulfonated and double sulfonated, the latter being much more expensive.

Sulfonated neatsfoot oil is sold with a 25 per cent moisture content. See comments on neatsfoot oil, which is itself widely adulterated.

Sulfonated olive oil is sold as 50 per cent (43 per cent fat), 75 per cent (63 per cent fat), and 80 per cent (68 per cent fat).

Sulfonated tallow is probably sulfonated at the unsaturated bonds of the oleo oil which is always present, or at the oleic radicals of the mixed glycerides. Grades are 35 per cent (24 per cent fat), and 50 per cent (48 per cent fat).

CHAPTER XXIII

AMINES, NITRO COMPOUNDS, AND VARIOUS ORGANIC NITROGEN DERIVATIVES

The amines and nitro compounds logically fall together because amines are usually obtained by reduction of nitro derivatives. Because of their interrelation other nitrogen derivatives, excepting proteins, are included. Amines may be primary, RNH_2, secondary, R_2NH or tertiary, R_3N. They form salts with acids, and in other ways have properties similar to those of inorganic bases, but are less reactive. The naming of the NH_2 compounds offers many difficulties. When the NH_2 group is attached directly to a hydrocarbon radical they are called **amines** or **amino compounds.** When the amino group replaces the hydroxyl of an acid, as in $RCONH_2$ from $RCOOH$, they are **amides** or **amido compounds.** The amides may be primary, secondary or tertiary as described for amines, but only primary amides are important commercially. There is a tendency to confuse nomenclature for amino and amido compounds, so that some names in commercial use do not strictly follow this scientific usage. Secondary amines and amides are sometimes called **imines** and **imides.** Nitro compounds sometimes drop an "o" in commercial nomenclature as nitraniline for nitroaniline. The latter is a preferred form.

All aromatic nitro and amino compounds are poisonous to some degree. To avoid repetition this will be noted only in cases where unusual caution is necessary.

Trichloronitromethane, nitrochloroform or **chloropicrin,** CCl_3NO_2, is a colorless liquid with an intense odor. It is only slightly soluble in water but mixes with alcohol or ether. Chloropicrin is prepared by mixing bleaching powder to a paste with cold water, adding picric acid and distilling. It is sold in cylinders of 185-pounds capacity and smaller, and is used as an insecticide and parasiticide, in organic synthesis, and as a war gas. It is a lachrymatory, and its inhalation produces severe headaches.

Hydroxylamine, NH_2OH, is the simplest ammonia derivative. In it one hydrogen has been replaced by an hydroxyl group. Commercially it is handled as the white crystalline salt, **hydroxylamine hydrochloride,** NH_2OH,HCl. It is a product of the reduction of ammonium chloride by powerful reducing agents, an electrolytic reduction being typical. Uses are as a strong reducing agent as in photographic developers, and in organic synthesis.

Methylamine, CH_3NH_2, is the simplest hydrocarbon substitution product of ammonia, in which one hydrogen has been replaced by the methyl group. It is readily produced by the treatment of methyl halides with ammonia under pressure. The same reaction gives secondary and tertiary amines, the quantity of each being controlled by conditions. Commercially it is sold as an aqueous solution containing about 35 per cent of the amine. The use of this in synthetic organic chemistry is limited because the higher boiling primary amines such as amylamine, are easier to handle.

Dimethylamine, $(CH_3)_2NH$, is the simplest secondary amine, produced as described under methylamine. It is a gas at room temperature, has the general odor of ammonia, and is very soluble in alcohol or water. It is sold as a liquid under pressure, or as a 25 per cent or 40 per cent aqueous solution. Uses are in organic synthesis and as a rubber accelerator.

Trimethylamine, $(CH_3)_3N$, is the simplest tertiary amine, produced as described under methylamine. It is a gas with a fishy odor, and is soluble in ether and very soluble in water or alcohol. Trimethylamine is sold in aqueous solution for use in synthetic organic reactions.

Diethylamine, $(C_2H_5)_2NH$, is a substitution product of ammonia in which two hydrogens have been replaced by ethyl groups. It is a colorless alkaline liquid produced, along with primary and tertiary amines, by treatment of ethyl halides with ammonia, under pressure. The alkaline liquid has an odor resembling that of ammonia, and is very soluble in water and soluble in alcohol or ether. It is relatively expensive, which limits its use in synthetic organic chemistry.

Monobutylamine or **butylamine,** $C_4H_9NH_2$, is a colorless liquid prepared by the reaction of the corresponding chloride with ammonia under pressure. It has an ammoniacal odor and mixes with water, alcohol or ether. Butylamine is used for organic synthesis, although the commercial material is a mixture, as indicated by its distilling over a range of about 20° C. **Dibutylamine,** $(C_4H_9)_2NH$, is similar but less soluble in water, and is used for similar purposes. **Tributylamine,** $(C_4H_9)_3N$, is a yellow liquid, almost insoluble in water but similar in other properties and in uses.

Amylamine or **monoamylamine,** $C_5H_{11}NH_2$, is a colorless liquid with an ammoniacal odor, soluble in water or alcohol and miscible with ether. It may be prepared along with the secondary and tertiary compounds by heating amyl chloride with ammonia under pressure. The product is recovered by fractionation from the mixed amines, and is a mixed material, since several isomeric amyl derivatives are present. It distils over a range of about 30° C. This contains over 90 per cent of mixed amines and is used in organic synthesis. Other uses are as a solvent for gums, resins and esters, as a corrosion inhibitor, and to form soaps used as wetting agents, emulsifying agents and lubricants. **Diamylamine,** $(C_5H_{11})_2NH$, is another mixture of isomers, which is a colorless to light yellow liquid. It is similar to the monoamine in many ways and is used for organic synthesis and as a solvent. **Triamylamine,** $(C_5H_{11})_3N$, is a mixture, also recovered from the mixed amines. The yellow liquid is insoluble in water but miscible with alcohol or ether. It also is used in organic synthesis, as an insecticide, and as a corrosion inhibitor. The fractionated amylamines are relatively expensive, and a commercial mixture containing about 60 per cent of monoamine and 40 per cent of diamine is sometimes substituted.

Triethanolamine, $(HOC_2H_5)_3N$, is a colorless to yellow liquid with an odor of ammonia. It is miscible with water or alcohol and soluble in ether. The product is prepared by the reaction of ethylene oxide and ammonia under pressure. Commercially it contains about 82.5 per cent of triethanolamine, 15 per cent of diethanolamine and 2.5 per cent of monoethanolamine. It is basic in nature and reacts with fatty acids to form soaps. Important uses are as an emulsifying agent, particularly in the form of its soaps, and for absorption of acid gases. It is a good wetting agent and is a form of very soluble aliphatic amine available at a reasonable price. **Diethanolamine,** $(HOC_2H_5)_2NH$, and **monoethanolamine,** $HOC_2H_5NH_2$, are also sold in somewhat impure form at somewhat higher prices. The mono compound is more alkaline than ammonia, the di compound intermediate between ammonia and the tri compound.

Aldehyde ammonia, $CH_3CH(OH)NH_2$, is the white crystalline product resulting from condensation of acetaldehyde and ammonia. It turns brown in the air, is very soluble in water or alcohol, and is slightly soluble in ether. The compound is an intermediate step in the preparation of pure acetaldehyde and is used as a rubber accelerator and in organic synthesis.

Acetamide or **acetic acid amide,** CH_3CONH_2, is a white deliquescent crystalline compound prepared by the reaction of ethyl acetate and ammonium hydroxide, or of ammonium carbonate and acetic acid. It is exceedingly soluble in water and very soluble in alcohol or ether. Acetamide frequently has an odor like that of mice from impurities usually present. Both C.P. and technical grades are available. The compound is used in organic synthesis.

Ethylene diamine, $C_2H_4(NH_2)_2$, is a colorless liquid soluble in water and organic solvents, and is typical of a large number of diamines which have not attained large commercial distribution. It is produced by reaction of ethylene dichloride with ammonia under pressure. It has a high alkalinity for its molecular weight, and is used as a neutralizing agent for special purposes, as a corrosion inhibitor, and in organic synthesis. **Morpholine,** $HN(C_2H_4)_2O$, is the similar structural derivative of ethylene oxide, higher in boiling point and of lower neutralizing value.

Phenylhydrazine hydrochloride, $C_6H_5NHNH_2.HCl$, is a colorless crystalline material prepared by reducing benzene diazonium chloride with stannous chloride and hydrochloric acid. It is very soluble in water and soluble in alcohol or ether. Grades sold are C.P., commercial and pure. This salt is used in organic synthesis as an expensive intermediate. It produces skin eruptions on exposure to it, and is merely a convenient form of handling the free base, **phenylhydrazine,** $C_6H_5NHNH_2$. The simple base **hydrazine,** H_2NNH_2 and its salt **hydrazine hydrochloride,** H_2NNH_2,HCl are relatively unimportant.

Urea or **carbamide,** $CO(NH_2)_2$, is a white crystalline compound extremely soluble in water, moderately soluble in alcohol, and slightly soluble in ether. It is prepared by heating ammonium cyanate, by heating ammonium sulfate and potassium cyanate, or by treating calcium cyanamide with dilute acid. The pure material is available for use in organic synthesis, the preparation of resins, etc. Domestic and imported grades containing 46 per cent of nitrogen are sold for use in fertilizers. **Thiourea,** $CS(NH_2)_2$, is similar but of lesser importance, as is also **guanidine,** $HNC(NH_2)_2$. The latter is much more expensive.

Barbital, veronal or **barbitone,** $(C_2H_5)_2C(CONH)_2CO$, is prepared by the reaction of the diethyl ester of malonic acid and carbamide. It may be considered as a substituted urea, **diethylmalonyl urea,** or as **diethylbarbituric acid.** It is a white, sublimable, crystalline compound slightly soluble in water, soluble in alcohol and very soluble in ether. The U.S.P. grade melts between 187° and 190° C. Aside from medical use as a sedative and hypnotic, it is reported to be a stabilizer for hydrogen peroxide, and to be used in plastics. **Soluble barbital, sodium barbital, sodium veronal** or **sodium barbitone** is **sodium diethylbarbitate** or **sodium diethylmalonyl urea,** $C_8H_{11}O_3N_2Na$. It contains 88-90 per cent of barbital according to U.S.P. standards, and is used medically in the same way as barbital.

Phenobarbital or **luminal** is **phenylethylbarbituric acid,** $(NHCO)_2{:}(CO){:}C{:}(C_2H_5)(C_6H_5)$, a white crystalline compound prepared by the condensation of urea with derivatives of phenylethylmalonic acid. It is very slightly soluble in water but very soluble in alcohol or ether. The U.S.P. grade melts between 173° and 177° C. and has the same medical use as barbital.

Diphenylguanidine, or **DPG,** $NH:C(NHC_6H_5)_2$, is prepared by treating aniline with cyanogen chloride. It is a white crystalline material, slightly soluble in water or ether, and moderately soluble in alcohol. DPG is used as an accelerator in the vulcanization of rubber.

Triphenylguanidine, $C_6H_5N:C(NHC_6H_5)_2$, is a white crystalline compound prepared by removing the sulfur from thiocarbanilide in the presence of aniline by heating in alcohol with lead monoxide. It is very soluble in ether or absolute alcohol, and is used as an accelerator in the vulcanization of rubber.

Diorthotolylguanidine, $CH_3C_6H_4NCNH_2NHC_6H_4CH_3$, is a white powder prepared by the removal of sulfur from diorthotoluolthiourea with lead monoxide in the presence of ammonium hydroxide. It is soluble in alcohol or ether and is used as a rubber accelerator.

Hexamethylenetetramine, methenamine, formin or **urotropin,** $(CH_2)_6N_4$, is a colorless crystalline material prepared by the reaction of ammonia with formaldehyde. It is extremely soluble in water, moderately soluble in alcohol. A U.S.P. grade 99 per cent pure, and a technical grade are sold. It is used in medicine as an antiseptic, and industrially as an absorbent for phosgene, as a rubber accelerator and in synthetic resin manufacture.

Nitrobenzene, nitrobenzol or **oil of mirbane** $C_6H_5NO_2$, is a light yellow, oily liquid of characteristic odor somewhat resembling that of oil of bitter almonds. It is slightly soluble in water and miscible with alcohol or ether. Nitrobenzene is produced by the reaction of nitric acid with benzene, preferably with sulfuric acid as a dehydrating agent. The double-distilled product is sold. Nitrobenzene is the starting point for the production of aniline, and therefore produced from benzene in tremendous quantities for use in the synthesis of organic chemicals. It is also used for its almond odor and for its solvent properties. For the latter applications it has been included in such products as metal polish, shoe polish, soaps, etc., for household use. In such cases its use is dangerous as it is highly poisonous, even by inhalation of the fumes. Therefore its inclusion in many products is now forbidden by law.

Aniline or **aniline oil,** $C_6H_5NH_2$, is **aminobenzene,** a colorless oil when freshly prepared, which rapidly turns to pink, red and brown in the air. It has a characteristic odor and is somewhat soluble in water and miscible with alcohol or ether. Aniline is prepared from nitrobenzene by reduction with iron filings and hydrochloric acid. After neutralizing excess acid with lime, the aniline is separated by distillation with steam. **Aniline for blue** or **aniline oil for blue** is pure aniline. **Aniline oil for red** is a mixture of aniline with *ortho-* and *para-***toluidine. Aniline for safranine** is a mixture containing *ortho-***toluidine.** Aniline is used in the preparation of many dye intermediates, as well as of synthetic organic products used in perfumes, drugs, etc. The former application is so general that the synthetic dyestuffs are popularly known as **aniline dyes.** Aniline is used to a limited extent as a solvent but is highly poisonous.

Aniline salt is **aniline hydrochloride,** $C_6H_5NH_2,HCl$, a white crystalline substance when pure, but usually pink to red. It is formed by crystallization from a solution of aniline in hydrochloric acid, and is soluble in alcohol, ether or water. Uses are in the manufacture of dyes, and in dyeing and printing where reaction occurs on the fabric. Other salts of aniline used more or less commercially are **aniline acetate,** $C_6H_5NH_2,$-HO_2CCH_3, and **aniline sulfate,** $(C_6H_5NH_2)_2,H_2SO_4$.

Formaldehyde aniline, $HCH(OH)NHC_6H_5$, is the dark brown liquid condensation product of formaldehyde and aniline. It is soluble in water or alcohol and is used as a rubber accelerator.

Dimethylaniline, $C_6H_5N(CH_3)_2$, is a yellow to brown oily liquid, insoluble in water but soluble in alcohol or ether. The odor resembles that of aniline. It is prepared by heating together aniline, anhydrous hydrochloric acid and methyl alcohol, or from aniline and methyl chloride. This material also results from heating chloro- or bromobenzene with dimethylamine at 250-260° C. It is an important dye intermediate, particularly as it is much less expensive than the ethyl homologue.

Ethyl aniline or **monoethyl aniline,** $C_6H_5NHC_2H_5$, is a colorless liquid turning brown on exposure to light. It is insoluble in water but miscible with alcohol or ether. Ethyl aniline has an odor like that of aniline, and is prepared by heating aniline and ethyl alcohol at 250° C. in the presence of sulfuric acid, or by heating ethyl bromide with aniline. It is used in organic synthesis.

Diethylaniline, $C_6H_5N(C_2H_5)_2$, is a yellow to brown liquid slightly soluble in water and soluble in alcohol or ether. The odor resembles that of aniline. It is prepared by heating together aniline, anhydrous hydrochloric acid and ethyl alcohol, or from chloro- or bromobenzene and diethylamine. Uses are in organic synthesis.

Ethylidene aniline, $C_6H_5N:CHCH_3$, is a dark brown liquid prepared by the reaction of acetaldehyde and aniline. It is soluble in water, alcohol or ether. The compound is an accelerator for the vulcanization of rubber and finds some use as a dye intermediate.

Ethylbenzylaniline, $C_6H_5N(C_2H_5)CH_2C_6H_5$, is a colorless to yellow or brown oily liquid very soluble in alcohol or ether. It is prepared by heating together benzyl chloride, ethyl aniline and sodium hydroxide solution. This is used in organic synthesis as in the manufacture of triphenylmethane dyes.

Diphenylamine or **phenylaniline,** $(C_6H_5)_2NH$, is a colorless to light yellow crystalline compound having a pleasant odor, prepared by heating aniline with aniline hydrochloride under pressure. It is very soluble in alcohol and soluble in ether. Diphenylamine is used as a dyestuff intermediate and as a stabilizer for nitrocellulose in explosives and celluloid.

Carbazole, $(C_6H_4)_2NH$, is diphenylimide, a white, crystalline, feebly basic compound separated from crude anthracene, or prepared by passing aniline vapors through a red hot tube. It is slightly soluble in alcohol, moderately soluble in ether. Grades sold are 70-80 per cent, 90 per cent, 95 per cent and 98.5-99 per cent. It is used in the preparation of dyes.

Acetanilide, phenyl acetamide or **antifebrin,** $C_6H_5NHCOCH_3$, is a white crystalline compound slightly soluble in water but very soluble in alcohol or ether. It is prepared by heating aniline with glacial acetic acid. Acetanilide is an important derivative of aniline, in which an amino hydrogen atom has been replaced by an acetyl group. A U.S.P. grade melting at 113-115° C., and a technical 95 per cent grade are sold. It is used as a stabilizer in hydrogen peroxide, as a rubber accelerator, in cellulose ester lacquers, in the manufacture of dyes and intermediates, and in medicines as an analgesic and antipyretic.

Acetoacetanilide or **acetylacetanilide,** $C_6H_5NHCOCH_2COCH_3$, is the colorless solid compound from the reaction of aniline and ethyl acetoacetate, or of aniline and diketene. The compound is soluble in ether, alcohol or chloroform and somewhat soluble in cold water. Its uses are as an intermediate in the synthesis of stable yellow organic pigments. Related chloroanilide and toluidide compounds are available for similar purposes.

***Para*-nitroacetanilide** or ***p*-nitroacetanilide,** $O_2NC_6H_4NHOOCCH_3$, is a colorless crystalline compound produced by acetylation of *para*-nitroaniline. It is soluble in alcohol or ether and slightly soluble in water. The product is an intermediate step in the manufacture of other derivatives, *para*-phenylenediamine being obtained by reduction and saponification.

***Para*-aminoacetanilide, *p*-aminoacetanilide** or **acetyl-*para*-phenylenediamine,** $NH_2C_6H_9NHOCCH_3$, is a colorless or reddish crystalline compound slightly soluble in water but very soluble in alcohol or ether. It is obtained by the partial acetylation of *para*-phenylenediamine, and is used for the preparation of intermediates and azo dyes.

***Ortho*-nitrochlorobenzene** or ***o*-nitrochlorobenzene,** $ClC_6H_4NO_2$, is a yellow liquid soluble in alcohol or ether. It is obtained along with the *para* isomer by nitration of chlorobenzene. They are separated by fractionation. ***Para*-nitrochlorobenzene** or ***p*-nitrochlorobenzene** is a yellow solid similar to the *ortho* compound. Both are dye intermediates, usually by conversion to the amino derivatives.

Ortho-**chloroaniline** or *o*-**chloroaniline,** $ClC_6H_4NH_2$, is a yellow oil miscible with alcohol or ether. It is prepared by reduction of *ortho*-nitrochlorobenzene with iron filings and hydrochloric acid for use as a dyestuff intermediate.

Ortho-**nitrophenol** or *o*-**nitrophenol,** $O_2NC_6H_4OH$, is a yellow crystalline compound, slightly soluble in water, very soluble in absolute alcohol or ether. It is formed together with *para*-nitrophenol when phenol is nitrated with dilute nitric acid at a low temperature. The mixture is washed and distilled with steam, when the *ortho*-compound distils over and the *para*-compound remains behind. It is used in organic synthesis. *Para*-**nitrophenol** or *p*-**nitrophenol,** $O_2NC_6H_4OH$, is a colorless crystalline compound which is much more soluble than the *ortho* compound. It is prepared from phenol with the *ortho* derivative for use in organic synthesis.

Ortho-**aminophenol** or *o*-**aminophenol,** $HOC_6H_4NH_2$, is the reduction product of *ortho*-nitrophenol by tin and hydrochloric acid. The white crystals are very soluble in ether, moderately soluble in alcohol and slightly soluble in water. It is used as a direct oxidation dyestuff, as an intermediate, and for photographic purposes.

Para-**aminophenol** or *p*-**aminophenol,** $H_2NC_6H_4OH$, is a light yellow to brown crystalline compound which turns violet on exposure to light. It is slightly soluble in water or ether and moderately so in alcohol. This product is prepared by the reduction of *para*-nitrophenol with iron filings or tin and hydrochloric acid. It is used as a photographic developer, by oxidation as a dye for fur, hair and leather, and is an intermediate for the preparation of other organic compounds.

Para-**aminophenol hydrochloride** or *p*-**aminophenol hydrochloride,** $HOC_6H_4NH_2,HCl$, is a white crystalline compound which darkens on exposure to air. It is very soluble in water and is prepared by the reaction of *para*-aminophenol with hydrochloric acid. This is used as a water-soluble form of *para*-aminophenol.

Picric acid or **2,4,6-trinitrophenol,** $HOC_6H_2(NO_3)_3$, is a yellow, crystalline solid, slightly soluble in cold water, moderately soluble in hot water or alcohol and very soluble in ether.

It is made by the direct nitration of phenol with mixed nitric and sulfuric acids. Picric acid is explosive and is usually sold with 10 per cent or 20 per cent of water for other uses. The U.S.P. grade melts at 121-3° C. It is applied as a treatment for burns and for other medical purposes. Picric acid is used as a yellow dyestuff, aside from use alone or in admixtures as an explosive.

Ortho-**nitro**-*para*-**chlorophenol** or *o*-**nitro**-*p*-**chlorophenol,** $HOC_6H_4(NO_2)Cl$, is the 1,2,4- derivative occurring as yellow crystals, very slightly soluble in water, soluble in alcohol and very soluble in ether. It is obtained by nitration of *para*-chlorophenol with dilute nitric acid or chlorination of *ortho*-nitrophenol. The nitration must be at low temperatures, preferably at −67° C. for the optimum yield of the product of the proper structure. It is a dye intermediate.

Ortho-**anisidine,** *o*-**anisidine** or *ortho*-**methoxyaniline,** $NH_2C_6H_4OCH_3$, is a yellow to red oily liquid prepared by reducing *ortho*-nitroanisole with iron filings and hydrochloric acid, or by heating *ortho*-aminophenol with potassium methylsulfate. It is very slightly soluble in water but very soluble in alcohol or ether. It is an intermediate for the manufacture of guaiacol and azo dyes.

Dianisidine or **dimethoxybenzidine,** $[C_6H_3(OCH_3)NH_2]_2$, is **di**-*para*-**aminodimethoxydiphenyl,** a crystalline compound prepared by reducing the methyl ether of *ortho*-nitrophenol in alkaline solution with zinc dust, and boiling the resulting hydrazo compound with hydrochloric acid. It is very soluble in alcohol or ether. Dianisidine is a dye intermediate.

Ortho-**nitrotoluene** or *o*-**nitrotoluene,** $CH_3C_6H_4NO_2$, is a yellow liquid prepared together with the *para*-nitro isomer, by nitration of toluene with nitric and sulfuric acids. The isomers are separated by fractional distillation. It is miscible with alcohol or ether and is used for the preparation of *ortho*-toluidine. *Para*-**nitrotoluene** or *p*-**nitrotoluene,** $CH_3C_6H_4NO_2$, is a yellow crystalline compound prepared as an isomer with the *ortho* compound. It is soluble in alcohol or ether and is used for the preparation of *para*-toluidine. The *para* isomer is much more expensive than the *ortho*. Mixed **nitrotoluenes** are relatively inexpensive. *Meta*-**nitrotoluene** or *m*-**nitrotoluene** is produced from *meta*-**nitrotoluidine** by the diazo reaction. The nitrotoluenes, both as a mixture and individually, are used in synthetic organic chemistry, largely in the manufacture of dyes and intermediates.

Xylidine, $H_2NC_6H_3(CH_3)_2$, is a liquid containing mixed isomers of the above formula, prepared by the nitration of commercial xylene and subsequent reduction with iron filings and hydrochloric acid. It is slightly soluble in water but very soluble in alcohol or ether, and is used as a dye intermediate.

Diethyl-*ortho*-toluidine or **diethyl-*o*-toluidine,** $H_3CC_6H_4N(C_2H_5)_2$, is the derivative of *ortho*-toluidine corresponding to diethylaniline. The toluidine derivative is produced by methods analogous to those used in producing the aniline derivatives from aniline. It is used in synthetic organic reactions.

Acetotoluidine or **acettoluidine,** $CH_3C_6H_4NHCOCH_3$, is prepared from mixed toluidines in the same way as acetanilide from aniline. It is soluble in alcohol or ether and is used as an antipyretic. **Acetyl-*p*-toluidine** or **acetyl-*para*-toluidine** is similarly prepared from *para*-toluidine for the same purpose.

Para-**toluene sulfonamide** or *p*-**toluene sulfonamide,** $CH_3C_6H_4SO_2NH_2$, is a white crystalline compound prepared by converting *para*-toluene sulfonchloride to the amide by treatment with ammonia. It is slightly soluble in water or ether and moderately so in alcohol. Uses are in organic synthesis.

Ortho-**ethyl**-*para*-**toluene sulfonamide** or *o*-**ethyl**-*p*-**toluene sulfonamide,** $C_2H_5C_6H_3(CH_3)SO_2NH_2$, is a white to light yellow crystalline material, slightly soluble in water or ether but more soluble in alcohol. It is obtained by the action of sulfur trioxide, or more conveniently chlorosulfonic acid, on *ortho*-ethyl-*para*-toluidine, and is a dye intermediate. **Ethyl**-*para*-**toluene sulfonamide** or **ethyl-*p*-toluene sulfonamide** is similar in properties to the previous isomer. It is obtained by treatment of *para*-toluidine as there outlined, followed by treatment of the product with ethyl chloride, and is a dye intermediate.

Saccharin or **benzoylsulfonic imide,** $C_6H_4COSO_2NH$, is a white crystalline compound, slightly soluble in water but soluble in alcohol or ether. It is manufactured from toluene by producing the sodium salt of toluene sulfonic acid, treating this with phosphorus pentachloride, distilling and cooling the residue, and centrifuging to separate the liquid *ortho* compound from the solid *para* compound. Treatment with mineral acid produces saccharin. The product is from 300 to 550 times as sweet as cane sugar and is used as a substitute for sugar. It sweetens without providing any food value, although it has some physiological action, and is used by diabetics.

Para-**toluene sulfonanilide** or *p*-**toluene sulfonanilide,** CH_3-$C_6H_4SO_2NHC_6H_5$, is a colorless to pink crystalline material soluble in ether and very soluble in alcohol. It is prepared by treatment of *para*-toluene sulfonchloride with aniline in the presence of lime, or of carefully regulated amounts of alkalies. It is a dyestuff intermediate.

Dinitrobenzene, $C_6H_4(NO_2)_2$, is a yellow crystalline material moderately soluble in absolute alcohol or ether. It is prepared by heating benzene with a mixture of nitric and sulfuric acids, or by longer heating with nitric acid alone. The chief product is *meta*-**dinitrobenzene** or *m*-**dinitrobenzene,** but small quantities of the *ortho* and *para* compounds are also formed. *Ortho*-**dinitrobenzene** or *o*-**dinitrobenzene** is recovered from the residues from the *meta* compound by solution in hot nitric acid and precipitation by dilution with water. *Para*-**dinitrobenzene** or *p*-**dinitrobenzene** can be similarly recovered but is also prepared by oxidation of *para*-quinaline dioxime. The dinitrobenzenes are used as intermediates for organic synthesis, particularly the *meta* compound, because it is easily and inexpensively prepared.

Ortho-**nitroaniline,** *o*-**nitroaniline** or *o*-**nitraniline,** $NO_2C_6H_4$-NH_2, occurs as orange crystals, slightly soluble in water and very soluble in alcohol or ether. It is prepared by heating *ortho*-dinitrobenzene with alcoholic ammonia, for use in organic synthesis.

Meta-**nitroaniline,** *m*-**nitroaniline** or *m*-**nitraniline,** NH_2-$C_6H_4NO_2$, is a yellow crystalline compound insoluble in water but moderately soluble in alcohol or ether. It is prepared by the acetylation of aniline, followed by nitration in the *meta* position and saponification of the acetyl ester. *Meta*-nitroaniline is used for the preparation of dyes and intermediates.

***Para*-nitroaniline, *p*-nitroaniline,** or ***p*-nitraniline,** $NH_2C_6H_4NO_2$, is a yellow crystalline compound moderately soluble in alcohol or ether, prepared by heating *para*-dinitrobenzene with alcoholic ammonia. It is used for the preparation of dyes.

***Para*-phenylenediamine, *p*-phenylenediamine, *para*-diaminobenzene** or **ursol D,** $C_6H_4(NH_2)_2$, is a colorless to red or brown crystalline compound which darkens on exposure to air. It is soluble in cold water, very soluble in hot, and very soluble in alcohol or ether. This is prepared by reducing *para*-dinitrobenzene with iron filings, or stannous chloride and hydrochloric acid. It is used for dyeing hair, furs, cotton, etc., by the production of a brown to black color, by direct oxidation with hydrogen peroxide or other oxidizing agent. It is also used as a dye intermediate and as a vulcanization accelerator.

***Meta*-phenylenediamine, *m*-phenylenediamine** or ***meta*-diaminobenzene,** $C_6H_4(NH_2)_2$, is a colorless crystalline compound very soluble in water, alcohol or ether. It is prepared by reducing *meta*-dinitrobenzene with iron filings or stannous chloride and hydrochloric acid. Uses are for the preparation of dyes and as an ingredient of direct-oxidation hair dyes.

Dinitrochlorobenzene, $ClC_6H_3(NO_2)_2$, is a colorless crystalline material prepared by the chlorination of commercial dinitrobenzene, which is mainly the *meta* product. The chlorine is therefore in the 2 or 4 position. It is soluble in alcohol or ether and is used as a dye intermediate.

Dinitrophenol, $HOC_6H_3(NO_2)_2$, is any one of, or a mixture of, three isomeric yellow crystalline compounds, prepared by nitrating phenol with mixed nitric and sulfuric acids. It is slightly soluble in water, soluble in alcohol, and very soluble in ether. Dinitrophenol is used in organic synthesis in the manufacture of dyes and other organic compounds such as amidol, and as a wood preservative.

***Meta*-nitro-*para*-toluidine** or ***m*-nitro-*p*-toluidine,** $H_3CC_6H_3(NO_2)(NH_2)$, is the 1,3,4- compound, a reddish crystalline material very slightly soluble in water but very soluble in alcohol.

It is obtained by boiling nitro-*p*-acettoluide with alcoholic caustic potash, and is a dyestuff intermediate.

Para-**nitro**-*ortho*-**toluidine** or *p*-**nitro**-*o*-**toluidine,** $H_3CC_6H_3(NH_2)(NO_2)$ is the 1,2,4- compound, the principal nitration product from *ortho*-toluidine. The brown crystals are soluble in alcohol or ether and are used for further synthetic reactions, such as reduction to the corresponding tolylenediamine.

Ortho-**tolidine** or **tolidine base,** $[C_6H_3(CH_3)NH_2]_2$ is a reddish crystalline compound slightly soluble in water but very soluble in alcohol or ether. It is prepared by the reduction of *ortho*-nitrotoluene with zinc dust in the presence of alkali, followed by treatment with hydrochloric acid, by the reduction of azotoluene with stannous chloride, or by treatment of hydrazotoluene with hydrochloric acid. The latter two methods are combined in the first one. Tolidine base and a distilled product are sold. It is used in dye synthesis.

Para-**nitrosodimethylaniline** or *p*-**nitrosodimethylaniline,** $ONC_6H_4N(CH_3)_2$, is produced from dimethylaniline by treatment with sodium nitrate in acid solution. The green crystals are soluble in alcohol or ether. It is an important intermediate in dye synthesis.

Benzidine or *para*-**diaminodiphenyl,** $(C_6H_4NH_2)_2$, has the form of silvery crystals and is prepared from nitrobenzene by reducing with zinc dust in alkaline solution or by electrolytic reduction of nitrobenzene. The free **benzidine base** is sold and is slightly soluble in water and soluble in alcohol. It is used as an intermediate in organic synthesis and as an important reagent. **Benzidine sulfate,** $(C_6H_4NH_2)_2.H_2SO_4$, is a white crystalline salt of benzidine which is only slightly soluble in water. It is also used in organic synthesis. Benzidine sulfonic acids are also sold.

Dinitrotoluene may theoretically be any one of three isomeric compounds, $CH_3C_6H_3(NO_2)_2$, prepared by the nitration of toluene with fuming nitric and sulfuric acids. It is obtained in the form of yellow crystals which are slightly soluble in water, moderately soluble in alcohol and very soluble in ether. If the isomers are present to an extent which tends to lower the melting point greatly, that is, much of the 2,4 and 3,4 compounds with the usual 3,5, it is quoted at a reduced price as an oily grade. It is an intermediate in the formation of other organic compounds and dyes. Added to dynamite, it lowers the freezing point of the nitroglycerine present. Further nitration gives **trinitrotoluene,** an explosive. The dinitro compound is not commonly used for that purpose.

Mixed toluidine, $CH_3C_6H_4NH_2$, is a light yellow to brown liquid mixture of the isomers having this formula, prepared by the reduction of mixed nitrotoluene with iron filings and hydrochloric acid. It is slightly soluble in water and miscible with alcohol or ether, and is used in organic synthesis and as a flotation oil. ***Ortho*-toluidine** or ***o*-toluidine** has the two substituted groups in the *ortho* position to each other, and is prepared by reducing *ortho*-nitrotoluene. This product is a light yellow liquid which darkens on exposure to the air. It is used in organic synthesis, as in the manufacture of dyes and saccharin. ***Para*-toluidine** or ***p*-toluidine** has the substituted groups in the *para* position. It is a white crystalline compound prepared by the reduction of *para*-nitrotoluene for use in the preparation of dyes and intermediates. The *para* isomer is much more expensive than the *ortho.*

***Meta*-tolylenediamine, *m*-tolylenediamine,** or **diaminotoluene,** $H_3CC_6H_3(NH_2)_2$, is a crystalline compound, very soluble in water, alcohol or ether. It is prepared by reducing *meta*-dinitrotoluene with iron filings or stannous chloride and hydrochloric acid. This is used as a dye intermediate and as a direct oxidation black for furs, hair, etc.

Methylene dianiline, $CH_2(NHC_6H_5)_2$, is a white to yellow pulverant solid. It results from the reaction of aniline and formaldehyde aniline, and is used as a rubber accelerator.

Thiocarbanilide or **sulfocarbanilide,** $(C_6H_5NH)_2CS$, is *α,β*-**diphenyl thiourea,** a colorless crystalline compound prepared by the reaction of aniline and carbon bisulfide. It is very soluble in alcohol or ether. Thiocarbanilide is used in organic synthesis. It was one of the earliest accelerators for the vulcanization of rubber and is still used for that purpose.

Picramic acid or **2-amino-4,6-dinitrophenol,** $HOC_6H_2(NH_2)(NO_2)_2$, is a reddish brown crystalline solid, slightly soluble in ether, moderately in alcohol, and very slightly in water. It is produced from picric acid by treatment with ammonium sulfide solution, and is used in the manufacture of azo dyes.

Para-**aminoazobenzene** or *p*-**aminoazobenzene,** $C_6H_5N:N\text{-}C_6H_4NH_2$, is the usual form of aminoazobenzene resulting from treatment of aniline with sodium nitrite in hydrochloric acid solution. The yellow to tan needles are very soluble in ether, benzene or hot alcohol but only slightly soluble in hot water. The compound is used in dyeing and as an intermediate in the preparation of azo dyes. The hydrochloride is known as **aminoazobenzene salt.** It forms blue needles and is soluble in alcohol. Uses are as an intermediate and as a color in lacquers. Mono and disulfonic acids of *para*-aminoazobenzene are also used as dye intermediates.

Ortho-**aminoazotoluene** or *o*-**aminoazotoluene,** $CH_3C_6H_4N:NC_6H_3(CH_3)NH_2$, is prepared similarly to aminoazobenzene as yellow to red crystals. It is soluble in alcohol, ether, and benzene, and is a dyestuff intermediate. **Aminoazoxylene** and **aminoazoxylidine** are structurally similar and similarly used.

Pyridine, $CH(CHCH)_2N$, is a tertiary amine. It is a colorless liquid having a disagreeable odor, soluble in ether and miscible with alcohol or water. This is prepared by the fractional distillation of a fraction of coal-tar oil. It is also produced from the dry distillation of animal and vegetable nitrogenous material. Denaturing and refined grades are quoted. The latter means that the distillation is cut within 2° C. It was formerly used for completely denaturing alcohol, a use which has declined greatly. Pyridine is a solvent for rubber, paint, varnish, etc., and is used as a textile assistant.

Synthetic musk is a name for a group of complex yellow crystalline synthetics soluble in alcohol, and used to replace natural musk. Three are commonly quoted, with distinctive forms of the names. **Musk xylene** or **musk xylol,** $C_4H_9(CH_3)_2C_6(NO_2)_3$, is prepared by reacting *meta*-xylene with butyl chloride in the presence of anhydrous aluminum chloride and then carefully nitrating. This is the most widely used, largely because it is the cheapest. **Musk ambrette,** $C_4H_9(CH_3)(OCH_3)C_6H(NO_2)_2$, is stronger and has a sweeter odor. *Meta*-cresol is first methylated to *meta*-cresylmethyl ether and then treated much as for musk xylene, but to a lower degree of nitration. **Musk ketone,** $C_4H_9(COCH_3)(CH_3)_2C_6(NO_2)_2$, is used to a much smaller extent than the other synthetic musks. It has a civet-like odor. Tertiary butyl-*meta*-xylene is prepared as for musk xylene. This is then reacted with acetyl chloride in the presence of aluminum chloride, and finally nitrated. All of these synthetic musks are used not only in perfumes but in noncitrus flavors such as strawberry, peach, currant, etc. There are other synthetic musks more restricted as to commercial availability.

Nitronaphthalene, $C_{10}H_7NO_2$, is a yellow crystalline compound prepared by the direct nitration of naphthalene with nitric and sulfuric acids. The *alpha* compound is the commercial product. It is soluble in alcohol and very soluble in ether. The main use is as an intermediate in the manufacture of dyes.

***Alpha*-naphthylamine** or **α-naphthylamine,** $C_{10}H_7NH_2$, is a white crystalline compound slightly soluble in water but very soluble in alcohol or ether. It turns red on exposure to the air. This is prepared by reducing *alpha*-nitronaphthalene with iron filings and acetic acid, followed by neutralization with lime water and distillation, and is used in the preparation of dyes. It is also used for toning photographic prints.

***Beta*-naphthylamine** or **β-naphthylamine,** $C_{10}H_7NH_2$, is a white to reddish crystalline compound, soluble in alcohol or ether and slightly so in water. It is prepared from *beta*-naphthol by heating with an aqueous solution of ammonia and ammonium sulfite at 120° C. in an autoclave. The product is also obtained by heating *beta*-naphthol with zinc ammonium chloride. A technical grade is sold as a dyestuff intermediate.

Phenyl-*alpha*-naphthylamine or **phenyl-α-naphthylamine,** $C_{10}H_7NHC_6H_5$, is the product of reaction of *alpha*-naphthylamine and bromobenzene heated in the presence of alkali. The yellow to white crystals are soluble in alcohol, ether or benzol and are used as a dye intermediate.

Dinitronaphthalene, $C_{10}H_6(NO_2)_2$, is a yellow, crystalline product, very soluble in ether. It is prepared by nitrating naphthalene with mixed sulfuric and nitric acids. The product is a mixture of 1,5- and 1,8- products and is used as a dye intermediate.

Hydroxyquinoline sulfate or **oxyquinoline sulfate,** $(C_9H_6NOH)_2,H_2SO_4$, is a yellow crystalline material prepared by mixing 8-hydroxyquinoline with sulfuric acid. It is very soluble in water, moderately so in alcohol and is used in medicine as an antiseptic.

Indole, indol, or **ketol,** $\underline{C_6H_4(CH)_2N}H$, is a white to yellowish, crystalline compound soluble in hot water and very soluble in alcohol or ether. It is prepared by the reduction of indigo blue, by heating *ortho*-nitrocinnamic acid with potassium hydroxide in the presence of iron filings, or by fusion of albumin with potassium hydroxide. Indole is also formed from proteins by putrefaction, and has a very disagreeable odor. It is feebly basic in character. A C.P. grade is sold for use in medicine and in jasmine, lilac and orange-blossom perfumes. It is very expensive.

Skatole or **skatol,** C_9H_9N, is **β-methyl indole,** a white crystalline compound with an obnoxious odor, formed by the putrefaction of proteins, and also by fusion of egg albumin with potassium hydroxide. It is soluble in alcohol or petroleum ether and is used in perfume in very small amounts. When diluted it resembles civet. It is very much more expensive than indole.

Antipyrine, phenazine, or **phenyldimethylpyrazolon,** $C_{11}H_{12}ON_2$, is prepared by the condensation of methylphenylhydrazine and ethyl acetoacetate. The white crystalline substance is very soluble in water or alcohol, slightly so in ether. The U.S.P. grade melts at 111-113° C. It is used in medicine as an analgesic, antipyretic and antirheumatic.

Amidopyrine, aminopyrine or **pyramidone,** $C_{13}H_{17}ON_3$, has the complex structure of **dimethylaminoantipyrine.** It is a white crystalline powder prepared by reducing isonitrosoantipyrine with zinc and methylating with methyl iodide. It is very soluble in alcohol and ether. The U.S.P. grade melts at 107-9°C., and is used in medicine as an anodyne and antipyretic.

Its use in preparations which may reach the public for general use is forbidden by law.

Cinchophen, $C_9H_5N(C_6H_5)(COOH)$, is **2-phenyl-quinoline-4-carboxylic acid,** a colorless to yellowish compound prepared by heating an alcoholic solution of aniline, pyruvic acid and benzaldehyde. It is slightly soluble in alcohol or ether. The U.S.P. X grade melting at about 210°C. is quoted, and is used in medicine for the treatment of gout and rheumatic fever. **Neocinchophen** is an ester. The same restrictions apply to their sale as to that of amidopyrine.

Hydrofuramide or **furfuramide,** $(C_5H_4O)_3N_2$, is a brownish yellow solid which is the product of reaction of furfural and ammonium hydroxide. It dissolves in chloroform, ether, alcohol, furfural and derivatives, acetone, aniline, etc., and is somewhat soluble in water and higher alcohols. Technical furfuramide is used in fungicides, in rubber accelerators and in resins.

Alpha-**aminoanthraquinone** or **α-aminoanthraquine,** $C_6H_4(CO_2)_2C_6H_3NH_2$, is the product of reduction of *alpha*-nitroanthraquinone in acid solution with zinc or iron. It forms red needles slightly soluble in alcohol and soluble in chloroform, acetone or benzene. Uses are as a dye intermediate, particularly in alizarine dyes. *Beta*-**aminoanthraquinone** or **β-aminoanthraquine** is similarly derived from the corresponding nitro compound. The properties are similar but the crystals are red to brown. It is used as a dye intermediate, particularly in indanthrene types.

CHAPTER XXIV

ESTERS

Esters may be considered as derivatives of acids in which the acid hydrogen atom has been replaced by an alkyl or aryl group. In the more familiar esters the acid portion is also organic, as in ethyl acetate, amyl lactate, benzyl benzoate, etc. These are the products of reaction of an acid and an alcohol with the loss of 1 molecule of water. Unlike the reaction of bases and acids this does not take place instantaneously nor is it made complete by simply mixing the ingredients. Examples of esters of inorganic acids are ethyl bromide and ethyl iodide, which have been considered here as halogen substituted hydrocarbons, ethyl nitrite, glycol boriborate, etc. Esters undergo hydrolysis in water, but the reaction is relatively slow. Many of the esters have marked characteristic odors which may play an important part in their usefulness.

Two definite groups of esters of organic acids are omitted from this chapter, the glycerides of fatty acids which are the saponifiable fats and oils—and the waxes, which are esters of high molecular weight alcohols with acids, usually fatty acids. Each forms a separate chapter.

The terminology of esters and ethers has been confused in the past, some esters having commercial names in which they are called ethers and some ethers having commercial names in which they are termed esters. Chemically the two are entirely separate and distinct.

The methods of preparation of esters are so uniform that a general description of the procedure will serve. Assuming the alcohol to be ROH and the acid R′COOH the reaction is $ROH + R'COOH \rightleftharpoons R'COOR + H_2O$. To carry this to completion it is necessary to absorb the water shown on the right hand side of the equation. If the ester is volatile it is usual to add sulfuric acid, which will absorb the water and which is nonvolatile, and then distil the ester. Thus ethyl acetate is produced by mixing ethyl alcohol, acetic acid and sulfuric acid, the ethyl acetate being then distilled. If, as occasionally occurs, the ester is not volatile, this procedure must be modified. In that case hydrogen chloride, often referred to as anhydrous hydrochloric acid, is added. This combines with the water and is distilled away as a constant-boiling mixture of hydrochloric acid and water, containing about 37 per cent of acid. The ester remaining behind has a purity dependent on the quality of the raw materials used, and the accuracy with which equivalent quantities were taken. Thus the raw materials for any ester are the corresponding alcohol and acid. In the exceptional case where this is not so, it is noted, such as for cellulose acetate, made from cellulose and acetic anhydride. Reaction of the alcohol with the anhydride of the acid is less common. No water is formed and no dehydrating agent is essential, although often used to take care of impurities of which water may be one.

Methyl formate, $HCOOCH_3$, is the simplest possible ester, that of formic acid and methyl alcohol. Methyl formate is miscible with alcohol, very soluble in water and soluble in many other organic solvents. The absolute composition is the same as that of acetic acid but the structure is different. The ester boils slightly above room temperature. Uses are in organic synthesis and in products used in fumigation.

Ethyl formate or **formic ether,** $HCOOC_2H_5$, is a limpid colorless liquid with an odor like that of benzaldehyde. It is moderately soluble in water and miscible with alcohol or ether. This ester is used medicinally, as an insecticide or larvicide, and in organic synthesis.

Amyl formate, $HCOOC_5H_{11}$, is **isoamyl formate.** The colorless liquid is soluble in alcohol or ether and is used in flavors and odors. It is usually about 90 per cent ester.

Benzyl formate, $HCOOCH_2C_6H_5$, is a clear, colorless liquid. It is miscible with alcohol or ether and used in perfumes and flavors.

Methyl acetate, CH_3COOCH_3, is a colorless, fragrant, limpid liquid, very soluble in water and miscible with alcohol or ether. Lead acetate may be added as a catalyst to the original esterification mixture of acetic acid, methyl alcohol and sulfuric acid. It is in general the best solvent among the members of the ester group. Domestic 99 per cent and 82 per cent grades are sold. The balance of the mixture is methyl alcohol, the lower concentration of ester forming a constant-boiling mixture of that composition. Both the synthetic product and that derived from wood distillation, are available as a solvent, in particular for nitrocellulose and cellulose acetate, and as a reagent in synthetic work. **Methyl acetone** is a mixture of 48 per cent acetone, 28 per cent of 82 per cent-grade methyl acetate, and 24 per cent methanol and is used as a solvent.

Ethyl acetate or **acetic ether,** $CH_3COOC_2H_5$, is a colorless liquid with an apple-like odor, moderately soluble in water and miscible with alcohol or ether. Impurities which may be present are free alcohol, free acetic acid, water and ether. The addition of 1 pint of a gasoline derivative, calol ethatate, per 100 gallons, is required by the Treasury Department to prevent its being used as an illegal source of ethyl alcohol. Acetic acid is removed by treatment with a solution of sodium carbonate, alcohol by treatment with a saturated aqueous solution of calcium chloride, and ether by fractional distillation. Anhydrous ethyl acetate is obtained by treating the ester with anhydrous calcium chloride, followed by distillation. Grades sold are ordinary and anhydrous. The ordinary grade is often quoted on the basis of ester content as 85 per cent and 95 per cent. Sometimes an attempt is made to distinguish acetic ether as the "best quality," a 99 per cent grade, but that terminology does not have general acceptance. The fragrant liquid is used in perfumery, flavoring products, medicine, as a solvent such as for phosgene, in making smokeless powders, artificial leather, nitrocellulose, lacquers and plastics, rayon, and artificial horsehair.

Isopropyl acetate, $CH_3COOCH(CH_3)_2$, is a colorless liquid, moderately soluble in water and miscible with alcohol or ether. It is a solvent for cellulose acetate and cellulose nitrate, and is used in lacquers because larger amounts of hydrocarbon diluents can be employed than with lower esters.

Butyl acetate, $CH_3COOC_4H_9$, enters the market as both **normal butyl acetate,** $CH_3COO(CH_2)_3CH_3$, and **secondary**

butyl acetate or **isobutyl acetate,** $CH_3COOCH_2CH(CH_3)_2$. Both are colorless liquids slightly soluble in water and miscible with alcohol or ether. They have fruity odors and are used in perfumes and flavoring extracts. Other uses are as solvents for gums, synthetic resins and cellulose acetate or nitrate. The secondary butyl product is less expensive. It is the major solvent of medium boiling point for lacquer formulation.

Amyl acetate, $CH_3COOC_5H_{11}$, is a mixed product, slightly soluble in water but miscible with alcohol or ether. The usual mixture contains mostly the isoamyl form, with some of the other isomers also present. It is sold in grades prepared from amyl alcohol from fusel oil, and from amyl alcohol from pentane. Normally it contains about 85 per cent of ester and 15 per cent of unesterified alcohols. The usual distillation range is about 30°C. The colorless liquid has a distinctive odor from which it has acquired the popular name of **banana oil.** It is used in many industries for its solvent properties, as for nitrocellulose, in making lacquers, photographic and moving picture films, in bronzing liquids and metallic paints, in making artificial pearls, and in the manufacture of celluloid, rayon, and perfumes. It is an important synthetic in pear and banana flavors. For perfume use, freedom from amyl alcohol is desirable. **Normal amyl acetate,** $CH_3COO(CH_2)_4CH_3$, and **secondary amyl acetate** or **isoamyl acetate,** $CH_3COOC(CH_2)_2$-$CH(CH_3)_2$, are isolated at a higher degree of purity. They are necessarily more expensive than the mixture because of rectification. Uses are similar.

Hexyl acetate, $CH_3COOC_6H_{13}$, is a colorless liquid, very soluble in alcohol or ether. The commercial product is made from secondary hexyl alcohol. It is a solvent for cellulose esters. **Octyl acetate, capryl acetate** or **2-ethyl hexyl acetate,** $CH_3COOCH_2CH(C_2H_5)C_4H_9$, is a colorless liquid soluble in alcohol. It is used as an odorant in perfumes and as a high-boiling solvent in lacquers, special inks, etc. The price permits reasonably general use.

Linalyl acetate, $CH_3COOC_{10}H_{17}$, is a colorless liquid very slightly soluble in water but miscible with alcohol or ether. It is isolated from bois de rose or shin oil. The odor resembles that of bergamot, and it is used in flavoring extracts, perfumery, Eau de Cologne, and soap. Varying grades according to ester content, such as 70 per cent and 90 per cent, are quoted.

Bornyl acetate and **isobornyl acetate,** $CH_3COOC_{10}H_{17}$, are similar to citronellyl acetate but have a pine odor. They are added to many odors. The isomeric compound is stronger, more persistent and less expensive than the normal bornyl compound.

Citronellyl acetate, $CH_3COOC_{10}H_{19}$, is an ester of the unsaturated alcohol citronellol from oil of citronella, rose, or geranium oil. The oily ester, soluble in alcohol or ether, is a powerful odorant resembling bergamot, and is much more expensive than the free alcohol.

Geranyl acetate, $CH_3COOC_{10}H_{17}$, is a colorless liquid, very slightly soluble in water but miscible with alcohol or ether. It is synthesized by the usual methods, and occurs in several essential oils. The odor resembles that of lavender or certain types of roses. The ester is used in perfumes and soaps. **Geranyl formate,** $HCOOC_{10}H_{17}$, and **geranyl butyrate,** C_3H_7 $COOC_{10}H_{17}$, are other esters of a rose type, similar in properties to the acetate but much more expensive.

Rhodinol acetate, is a mixture of about two parts of citronellyl acetate and one part of geranyl acetate, resulting from acetylation of rhodinol. It is soluble in alcohol or ether, and used largely in rose compounds. **Rhodinol formate** and **rhodinol butyrate** are similar esters of the corresponding acids and are similarly used.

Terpinyl acetate, $CH_3COOC_{10}H_{17}$, is a colorless liquid, miscible with alcohol or ether. It is purified by distillation, to over 98 per cent of ester. The odor is that of bergamot. It is used to replace oil of bergamot in Eau de Cologne, lavender water, inexpensive perfumes and soaps.

Acetin, monoacetin or **glyceryl monoacetate,** $CH_3COOC_3H_5(OH)_2$, is a colorless, viscous, hygroscopic liquid, very soluble in water, alcohol or ether. It is formed by heating glycerine with acetic acid, distilling off the dilute acetic acid, and again heating with glacial acetic acid and distilling. Free acetic acid may remain as an impurity. The technical grade is used for gelatinizing smokeless powders, treating dynamite to make it noncongealing, in the production of dinitroacetylglycerine, in tanning, and as a solvent for basic dyes.

Triacetin or **glyceryl triacetate,** $(CH_3COO)_3C_3H_5$, is prepared by the reaction of acetic anhydride with glycerine. The colorless odorless oil is moderately soluble in water and miscible with alcohol or ether. It is used as a fixative in perfumery and as a camphor substitute in pyroxylin. The technical grade contains substantial amounts of **glyceryl monoacetate** and **glyceryl diacetate.**

Ethylene glycol monoethyl ether acetate, $CH_3COOCH_2CH_2OC_2H_5$, is the ester of ethyleneglycol monoethyl ether. It is a colorless liquid, very soluble in water, alcohol or ether. Due to its mixed properties of an ether and an ester it is both a plasticizer and a solvent for nitrocellulose and cellulose acetate in lacquers and plastics. The corresponding **ethylene glycol monomethyl ether acetate,** $CH_3COOCH_2CH_2OCH_3$, **ethylene glycol monobutyl ether acetate,** $CH_3COOCH_2CH_2OC_3H_5$, and **diethylene glycol monoethyl ether acetate,** $CH_3COOCH_2CH_2OCH_2CH_2OC_2H_5$, are similar in properties and uses.

Sucrose octaacetate is a white crystalline ester of sucrose, cane sugar. It is nearly insoluble in water but soluble in coal-tar hydrocarbons, acetone, alcohol, etc. Grades sold are technical and denaturing. It is used as a plasticizer in adhesives and other products, as a waterproofing agent, etc. Its solutions are extremely bitter and therefore it is one of the denaturants used in alcohol when the latter is sold freely to the public, as in denatured alcohol.

Cellulose acetate is formed by the reaction of cellulose and acetic anhydride in the presence of sulfuric acid. It is usually a mixture of cellulose esters. **Cellulose triacetate,** $[C_6H_7O_2(OOCCH_3)_3]_n$, is soluble in glacial acetic acid. **Cellulose tetraacetate,** $[C_6H_6O(OOCCH_3)_4]_n$, is soluble in methyl alcohol. **Cellulose pentaacetate,** $[C_6H_5(OOCCH_3)_5]_n$, is soluble in alcohol. The pentaacetate is usually formed first and hydrolyzed back to the desired degree. The processes are diverse in different plants. An acetone-soluble grade can be obtained. The material is sold as a fluffy powder or in flake form, and is white to light yellow. Unlike the other commercially important cellulose ester, nitrocellulose or cellulose nitrate, it is not highly inflammable, although it is combustible.

Cellulose acetate is used in making acetate rayon, noninflammable photographic and moving-picture film, lacquers, varnishes, shatter-proof glass, plastics, rubber substitutes, and in rendering textiles and leather noninflammable and resistant to water. Commercially it is of importance not only as a chemical but also in the form of sheets, rods, tubes, etc. Cellulose acetate sheeting is a competitor of the viscose sheeting known as **cellophane.** Its importance is constantly increasing.

Cellulose acetobutyrate, is a mixed ester of cellulose with acetic and butyric acids. In general it resembles cellulose acetate. While somewhat more expensive than the acetate it has advantages of solubility due to the larger molecular-weight acid replacing part of the acetic acid.

Benzyl acetate, or **phenylmethyl acetate,** $CH_3COOCH_2C_6H_5$, is very slightly soluble in water, and miscible with alcohol or ether. It is present to about 65 per cent in oil of jasmine, as well as in lesser amounts in gardenia, narcissus, etc. Aside from the usual methods, it can be prepared by the reaction of benzyl chloride and sodium acetate. The colorless liquid is sometimes contaminated with chlorine, which detracts from its flowery jasmine-like odor. It is used in perfumes and flavoring products, and as a solvent for cellulose acetate and cellulose nitrate. Its use as a high-boiling solvent is necessarily limited because of its high price.

Phenylethyl acetate, $CH_3COOC_2H_4C_6H_5$, is the colorless liquid ester of phenylethyl alcohol and acetic acid. It is soluble in ether and has an odor resembling that of rose and peach. Use is as an odorant.

Styralyl acetate or **methyl phenyl carbinol acetate,** $CH_3COOCH(CH_3)C_6H_5$, is an expensive ester derived from oil of gardenia. It is colorless and soluble in alcohol. Uses are mainly in gardenia and lily perfumes.

Isobutylphenyl acetate, $CH_3COOCH_2C(CH_3)_2C_6H_5$, is similar to benzyl acetate in properties, but is used in rose, sweet pea and other sweet perfumes for its honey-like odor.

Ethyl propionate, $CH_3CH_2COOC_2H_5$, is a colorless liquid, slightly soluble in water but miscible with alcohol or ether. It is used in fruity types of flavors and odorants.

Butyl propionate, $CH_3CH_2COOC_4H_9$, is a colorless liquid very slightly soluble in water, and miscible with alcohol or ether. Butyl alcohol and other esters may be present as impurities. The colorless liquid is used as a high-boiling solvent for nitrocellulose. **Amyl propionate,** $CH_3CH_2COOC_5H_{11}$, is a colorless ester miscible with alcohol or ether, made from fusel oil and propionic acid, and used as a solvent in lacquers. In highly refined form it is an odorant and flavor, particularly for jasmine and peach.

Benzyl propionate or **benzyl methyl propionate,** C_2H_5-$COOCH_2C_6H_5$, is similar to benzyl acetate but sweeter in odor. It is much more expensive.

Phenylethyl propionate, $C_2H_5COOC_2H_4C_6H_5$, is similar to phenylethyl acetate but has a dried rose-petal odor.

Methyl lactate, $CH_3CHOHCOOCH_3$, is a colorless liquid usually containing up to 5 per cent of alcohols. It is soluble in nearly all organic solvents and is used as a cellulose acetate solvent.

Ethyl lactate, $CH_3CHOHCOOC_2H_5$, is a colorless liquid miscible with water, alcohol or ether. Aside from the usual esterification methods, it is produced by reaction of acetaldehyde with hydrocyanic acid to form **acetaldehyde cyanhydrin,** which by treatment with ethyl alcohol and hydrochloric acid forms the product. It is used as a solvent for cellulose acetate and nitrocellulose, and in medicine. **Butyl lactate,** CH_3-$CHOHCOOC_4H_9$, is a colorless liquid, slightly soluble in water but miscible with alcohol or ether. It is used as a solvent for cellulose esters and in perfumes. **Amyl lactate** is commercially **isoamyl lactate,** $CH_3CHOHCOOC_5H_{11}$. It is a colorless to light yellow liquid soluble in alcohol or ether, and is used as a solvent and plasticizer for cellulose esters.

Ethyl butyrate or **butyric ether,** $C_3H_7COOC_2H_5$, is slightly soluble in water and soluble in alcohol or ether. The colorless liquid has an odor resembling that of pineapple, and is used in flavoring extracts and inexpensive perfumes, particularly the theater-spray type.

Amyl butyrate is commercially **isoamyl butyrate,** C_3H_7-$COOCCH_2CH(CH_3)_2$. The colorless liquid, miscible with alcohol or ether, is used in flavoring compounds, largely to simulate apple or pineapple. It is also used in perfumes, particularly for spraying.

Ethyl oxybutyrate or ethyl hydroxybutyrate, $(CH_3)_2$-$C(OH)COOC_2H_5$, is a colorless liquid soluble in alcohol or ether. It is an isobutyl derivative used as a solvent for cellulose esters.

Benzyl butyrate, $C_3H_7COOCH_2C_6H_5$, is a liquid ester soluble in alcohol or ether. It has a heavy fruity odor and is used for blending in odorants and flavorings.

Ethyl valerianate, ethyl valeriate or **valerianic ether,** $C_4H_9COOC_2H_5$, is a colorless liquid, slightly soluble in water and miscible with alcohol or ether. It is used in flavors and odorants. **Amyl valerianate** or **amyl valerate,** $C_4H_9COOC_5H_{11}$, is similar.

Methyl acetoacetate, $CH_3COCH_2COOCH_3$, is a colorless transparent liquid produced by the reaction of methyl acetate and methyl alcohol in the presence of sodium. It is less important than ethyl acetoacetate and is used for similar purposes.

Ethyl acetoacetate, acetoacetic ester or **diacetic ester,** CH_3-$COCH_2COOC_2H_5$, is produced from ethyl acetate and acetic acid by reaction with sodium. It is a colorless to light yellow liquid with a fruity odor, very soluble in alcohol, soluble in many other organic solvents and slightly soluble in water. This ester is highly reactive and forms a basis for the so-called acetoacetic-acid synthesis reactions; and is used in the preparation of drugs such as antipyrine, perfume materials such as ionone, dyestuffs, etc.

Amyl caproate or **isoamyl caproate,** $C_5H_{11}COOC_5H_{11}$, is a colorless to light yellow ester, soluble in alcohol or ether, and used in perfume and flavors.

Ethyl crotonate, $CH_3CH:CHCOOC_2H_5$, is a colorless liquid with a pleasant odor. It is miscible with alcohol or ether and is used in perfumes.

Ethyl caproate, $C_5H_{11}COOC_2H_5$, is a yellow to colorless liquid with a pleasant odor, and is soluble in alcohol or ether. It is used in making artificial fruit essences and in organic synthesis.

Butyl oleate, $CH_3(CH_2)_7CH:CH(CH_2)_7COOC_4H_9$, is a light yellow liquid miscible with alcohol or ether. It is a plasticizer for lacquers and nitrocellulose plastics. **Amyl oleate,** $CH_3(CH_2)_2CH:CH(CH_2)_7COOC_5H_{11}$, is a light yellow liquid ester useful as a high-boiling plasticizer having solvent properties for nitrocellulose.

Amyl stearate, or **isoamyl stearate,** $CH_3(CH_2)_{16}COOC_5H_{11}$, is a colorless to pale yellow liquid which is not solely the isoamyl derivative. This ester is very soluble in alcohol or ether. It is distillable at reduced pressures and usually contains a small excess of stearic acid, about 1-2 per cent. It is used as a high-boiling solvent and plasticizer for cellulose esters.

Triethanolamine oleate or **trihydroxyethylamine oleate,** $(HOC_2H_4)_3NHOOCC_{17}H_{33}$, and **triethanolamine stearate** or **trihydroxyethylamine stearate,** $(HOC_2H_4)_3NHOOCC_{17}H_{35}$, are soaps of triethanolamine which are available on the market to meet a small demand. They are also readily made by reaction of triethanolamine with the corresponding fatty acid. Uses are largely as emulsifying agents.

Glyceryl stearate or **glyceryl monostearate,** $C_{17}H_{35}COOC_3H_5(OH)_2$, is an unctuous white solid, a monostearate of glycerine, the tristearate being tallow. It is both a fat and an alcohol and is used in cosmetics, in textile finishes, and as an emulsifying agent.

Diglycol laurate, $C_{11}H_{23}COOC_2H_4OC_2H_4OH$, is a light yellow, liquid ester soluble in alcohol or ether, and used in cosmetics, textile finishes, etc. It is structurally related to glyceryl stearate.

Diglycol oleate, $C_{17}H_{33}COOC_2H_4OC_2H_4OH$, is a light yellow to brown liquid ester soluble in alcohol or ether and slightly soluble in water. It is used in cosmetics, polishes, insecticides, and textile specialties, as a wetting and emulsifying agent.

Diglycol stearate, $C_{17}H_{35}COOC_2H_4OC_2H_4OH$, is a white to brown, unctuous solid. It is soluble in alcohol or ether and used in cosmetics, as a lubricant for dies, and as an emulsifying agent in varied products.

Ethyl oxalate or **diethyl oxalate,** $(COOC_2H_5)_2$, is decomposed by water but miscible with alcohol or ether. The colorless aromatic liquid is used in organic synthesis, particularly that of tartrazine and phenobarbital. It is also a lacquer solvent of limited applicability because of its high price. **Butyl oxalate** or **dibutyl oxalate,** $(COOC_4H_9)_2$ and **amyl oxalate** or **diamyl oxalate,** $(COOC_5H_{11})_2$, are colorless liquid esters of oxalic acid and the corresponding alcohols. Properties, prices and uses are similar to those of the ethyl compound.

Butyl tartrate or **dibutyl tartrate,** $(HOCHCOOC_4H_9)_2$, is very soluble in alcohol or ether. It is a colorless liquid freezing at about room temperature, used as a plasticizer for plastics and lacquers. Both domestic and imported grades are quoted, the latter being much more expensive.

Tributyl citrate, $C_3H_4(OH)(COOC_4H_9)_3$, is a light yellow liquid with but a trace of odor. It is soluble in several organic solvents. Uses are as a plasticizer for cellulose acetate and solvent for nitrocellulose.

Tributyl phosphate, $(C_4H_9)_3PO_4$, is a colorless to light yellow liquid used as a plasticizer in nitrocellulose plastics and in lacquers.

Triamyl borate, $(C_5H_{11})_3BO_3$, is a colorless liquid, soluble in alcohol or ether, and used for wetting and dispersing pigments. It is obtainable by the direct heating of boric acid and amyl alcohol.

Glycol boriborate, is a liquid of somewhat indefinite composition. It is the product obtained by heating glycol, sodium borate and boric acid, and is a light yellow liquid soluble in cold water, easily soluble in hot water and in absolute alcohol, glycerine and other alcohols. It is an adhesive, a binder for compounds to be fixed by heating, a softener for fabrics and a fire retardant. **Glycerol boriborate** or **glycerine boriborate,** is similar in properties to glycol boriborate.

Ethyl carbonate or **diethyl carbonate,** $(C_2H_5)_2CO_3$, is formed synthetically. Phosgene and ethyl alcohol react to form **ethyl chlorocarbonate,** $C_2H_5CO_2Cl$, which reacts with anhydrous ethyl alcohol to give the product. This is redistilled to give a colorless liquid of ethereal odor, miscible with alcohol or ether. Both commercial or 90 per cent, and a 99 per cent refined grade are available. The ester is used as a solvent and plasticizer in lacquers and plastics, and in organic synthesis. The intermediate, ethyl chlorocarbonate is also sold as a colorless liquid soluble in alcohol or ether, and used as a reagent in organic synthesis. It is usually about 90 per cent pure.

Methyl heptine carbonate or **methyl heptyne carbonate,** $C_5H_{11}CH:CHCOOCH_3$, is a colorless oily liquid having an unpleasant odor. It is insoluble in water but miscible with alcohol or ether. This ester is expensive and is used in perfume for violet tones. **Methyl octine carbonate,** $C_6H_{13}CH:CHCOOCH_3$, is similar in structure and properties but more pungent.

Ethyl nitrite or **nitrous ether,** $C_2H_5NO_2$, is a colorless to yellowish, highly volatile, inflammable, oily liquid prepared by the action of nitrogen trioxide on ethyl alcohol, or by treating alcohol with sodium nitrite and sulfuric acid. It is miscible with alcohol and soluble in ether. Uses are in the preparation of other organic compounds and in medicine. U. S. P. **spirit of ethyl nitrite** is an alcoholic solution containing 3.5-4.5 per cent of the ester. **Amyl nitrite** or **isoamyl nitrite,** $C_5H_{11}NO_2$, is a clear yellow, highly inflammable liquid with a fruity odor and aromatic taste, which is miscible with alcohol or ether. It is prepared in the same way as ethyl nitrite, and is used in medicine, or occasionally in organic synthesis.

Ethyl silicate or **tetraethyl orthosilicate,** $(C_2H_5)_4SiO_4$, is a colorless liquid with but little odor. It is one of the very few compounds of orthosilicic acid and is obtained by the reaction of alcohol and silicon tetrachloride or of sodium ethylate and silicon tetrafluoride. This is soluble in water with slow hydrolysis to ethyl alcohol and silicic acid. Uses are for the hardening of stone surfaces, in fireproof paints, and in other cases where it is desired to produce silicic acid *in situ* such as in mortars, molding compounds, etc.

Methyl sulfate or **dimethyl sulfate,** $(CH_3)_2SO_4$, is a colorless to yellow liquid, with an ethereal to definitely unpleasant odor, depending on impurities. It is produced by the reaction of fuming sulfuric acid and methyl alcohol, and is soluble in alcohol or ether. Hot alcohol decomposes it. Uses as a reagent in organic synthesis are largely as a higher-boiling substitute for methyl halides. **Ethyl sulfate** or **diethyl sulfate,** $(C_2H_5)_2SO_4$, is similar in preparation and properties, and is used in place of ethyl halides.

Diamyl sulfide, $(C_5H_{11})_2S$, is a yellow mixture of various isomeric amyl derivatives produced by reaction of amyl chloride with alcoholic potassium sulfide. It is a synthetic-organic reagent.

Nitrocellulose is a mixture of cellulose nitrates obtained by treating cellulose with nitric acid in the presence of sulfuric acid. The term nitrocellulose, which is almost universally used, implies a nitro-compound structure but the true structure is that of **cellulose nitrate,** for which the formula $(C_6H_6(NO_3)_6)_n$, would represent the highest possible degree of nitration. Various degrees of nitration and differing types of products are obtained according to the concentration of acid used, temperature and time of reaction. The solubility of the products also varies according to the degree of nitration, those having the highest nitrogen content being insoluble in an ether-alcohol mixture, those with a lower nitrogen content being soluble. The subject is further complicated by the low viscosity of solutions of cellulose nitrate when a high degree of nitration has been followed by acid hydrolysis with acetic acid. This type is the so-called "**low-viscosity cotton.**" The nitrogen content of nitrocellulose may vary from 6-7 per cent to 13-13.5 per cent.

The highest degree of nitration yields a product used as guncotton in explosives. While an article of commerce, it is not freely available. Products containing less nitrogen still vary considerably among themselves. The higher proportions of nitrogen give nitrocelluloses used in smokeless powder and dynamite, and therefore still restricted as to sale. The nitrocellulose of commerce will stand heating to 135°C. without decomposition, as detectable by methyl violet paper. This material is shipped wet with 30 per cent of denatured alcohol, and so long as it does not dry, is not considered more dangerous than the alcohol with which it is moistened. The nitrocellulose manufacturer also often ships nitrocellulose with part or all of the solvents desired by the purchaser, billing for each separately. The solvents used are constantly changing to meet modifications in the art of producing lacquers.

The viscosity of nitrocellulose is almost universally used for its classification, expressed in terms of time in seconds for the fall of a standard ball through the solution under standard conditions. Any consideration of the method requires description of the instrument. The standard glass tube is 14 inches long and 1 inch in diameter. Marks are etched on the tube approximately 2 inches from each end, thus setting off a length of 10 inches. One end is closed with a cork stopper. The standard ball is a 5/16-inch ball bearing with a weight of approximately 2.04 grams. Temperature is standardized at 25°C. The solution used is as follows: 12.2 per cent of nitrocellulose, 22.0 per cent of denatured ethyl alcohol containing 5 per cent of methanol, 17.5 per cent of ethyl acetate, and 48.3 per cent of toluene. For a half-second nitrocellulose, this is modified to 20, 20, 16 and 44 per cent, respectively, and for quarter-second nitrocellulose to 25, 18.7, 15.0 and 41.3 per cent. The nitrocellulose so used must be dried, usually by hot air at 65-75°C. When overheated, nitrocellulose in any degree of nitration may explode. The time in seconds multiplied by 3.77 gives viscosity in poises. The method is only accurate to about 5 per cent.

Pyroxylin is another term for nitrocellulose and is commonly applied only to products of a degree of nitration below the explosive grade, more particularly to tetranitrocellulose. Important forms are sheets, rods, film, etc. **Pyroxylin lacquer** is a solution of pyroxylin in suitable solvents. It is relatively unimportant because the concentration of solids is low.

Collodion is a U.S.P. preparation containing 40 grams of pyroxylin per liter in a mixture of 3 parts of ether to one part of alcohol by volume. **Flexible collodion** consists of 20 grams of camphor and 30 grams of castor oil dissolved in collodion, and diluted to one liter with the collodion. It is also U.S.P. These collodions are used mainly for coating molds, but the compositions differ but little from those used in many other ways. Special collodions are also available. Alcohol-soluble grades of nitrocellulose are sold at ½-second and 40-second viscosities. Bronzing nitrocellulose is sold at viscosities of 30, 40 and 70 seconds. The ester-soluble grade most used in lacquers is sold at viscosities of ¼, ½, 5-6, 15-20, 20-30 and 60-80 seconds.

Quarter-second nitrocellulose and **half-second nitrocellulose** are used for the manufacture of lacquers for application by spray or brush. Alcohol-soluble grades enter into products where a high content of anhydrous alcohol is desired in the solvent. Higher-viscosity nitrocellulose is similarly used where a thinner film is desired. Some higher-viscosity nitrocellulose is used for wood lacquers. **Dope nitrocellulose** is a 15-second grade, and is used for clear and pigmented lacquers with large gum contents, for bodying other nitrocelluloses, and to waterproof shellac. Such nitrocelluloses for lacquer use are sometimes called **soluble cotton.** **Bronzing nitrocellulose** is specially prepared to hold bronze powders in solution without gelation. **Silver lacquer nitrocellulose** is a 20-second grade used for coating polished silver articles. **Nitrocellulose emulsions** are nitrocellulose solutions in solvents, dispersed in water as an emulsion.

Celluloid scrap or **pyroxylin scrap** is the material left when the original celluloid blocks are cut or sawed into useful articles. Some rejects from molding operations fall in this class. **Celluloid shavings** or **pyroxylin shavings** are similar. They consist of nitrocellulose with camphor or equivalent plasticizer. The scrap is sold as mottled, amber, black, colored, transparent, ivory, gray, etc., and the shavings as amber, mixed-colored and white. Prices vary widely from the transparent or highest price to mixed or cheapest grades. The scrap is used as a cheap substitute for nitrocellulose in adhesives, lacquers where low viscosity is not essential, some plastics, etc.

Film scrap consists of celluloid cuttings of used or discarded film from which the emulsion has been removed for recovery of its silver content. Grades sold are water white, light colored and dark colored. It is used in much the same way as celluloid scrap, with which it is competitive in price. Sheets recovered from used X-ray films by removal of the photographic emulsion from the surface are also an article of commerce but are re-used in making novelties such as buttons, license holders and ornaments, and are not sold as film scrap.

Methyl benzoate, essence of Niobé, or **oil of Niobé,** C_6H_5-$COOCH_3$, is miscible with alcohol or ether. It is a colorless liquid, occurs in several essential oils and is used in perfumes. In flavors it has the general taste of currants. **Ethyl benzoate,** $C_6H_5COOC_2H_5$, and **isobutyl benzoate,** $C_6H_5COOCH_2CH$-$(CH_3)_2$, are similar to methyl benzoate, slightly more expensive, sweeter in tone and not as strong. **Amyl benzoate,** is normally **isoamyl benzoate,** $C_6H_5COOC_5H_{11}$, a colorless liquid soluble in alcohol. The odor resembles that of ambergris. The ester is used in perfumes as a fixative and in soaps with new-mown hay odors.

Benzyl benzoate, $C_6H_5COOCH_2C_6H_5$, is soluble in alcohol and miscible with ether. It is prepared by the reaction of sodium benzoate and benzyl chloride, by esterification of benzoic acid with benzyl alcohol, or by treating benzaldehyde with alcoholic potassium hydroxide. The colorless liquid is sometimes contaminated with benzaldehyde. It is used as a perfume fixative and a solvent for musk, as an expensive solvent for cellulose acetate or nitrocellulose in suitable products, to replace camphor in celluloid, in medicine, and in flavors for candy and chewing gum.

Beta-**naphthol benzoate, β-naphthol benzoate** or **benzonaphthol,** $C_6H_5COOC_{10}H_7$, is prepared by the reaction of benzoyl chloride and *beta*-naphthol. The white crystalline powder is soluble in hot alcohol or in chloroform. It is used in medicine.

Methyl salicylate, $HOC_6H_4COOCH_3$, is a colorless, yellowish or red-brown liquid, soluble in alcohol and miscible with ether. Aside from esterification reactions for its synthesis, it is distilled from the leaves of *Gaultheria procumbers* or the bark of *Betula lenta.* The U.S.P. standard requires 98 per cent purity and labeling as to source. It has the odor and flavor of wintergreen and is used in perfumery and flavoring materials, and in medicine. Because of its relatively low cost it is added as a "cover-odor" to many industrial products, added to many perfumes, and used particularly in perfume sprays.

Amyl salicylate is **isoamyl salicylate,** $HOC_6H_4COOC_5H_{11}$, a colorless to yellow oil, very soluble in alcohol and miscible with ether. Lower esters and free isoamyl alcohol are sometimes present as impurities but grades over 99 per cent pure are available. The odor is variously described as that of orchids or clover. It is used in perfumes as an odorant and fixative, especially for soaps, and in medicine. The odor is very persistent. **Isobutyl salicylate,** $HOC_6H_4COOCH_2CH(CH_3)_2$, is similar in properties but has more body and is much more expensive.

Phenyl salicylate or **salol,** $HOC_6H_4COOC_6H_5$, is a white crystalline material, very soluble in alcohol and extremely so in benzene. It is prepared by heating salicylic acid and phenol in the presence of phosphorus pentachloride as a dehydrating agent. The product has a slight aromatic odor. U.S.P. granular or powdered grades melting at 41-3°C. are used in medicine and as a preservative.

Benzyl salicylate, $HOC_6H_4COOCH_2C_6H_5$, is a white crystalline ester, very soluble in alcohol. It is a fixative for perfumes and a solvent for musks. It is used particularly with carnation, jasmine and lilac blends.

Menthyl salicylate, $HOC_6H_4COOC_{10}H_{19}$, is a colorless, oily liquid with a menthol odor. It is soluble in alcohol or oils, and contains considerable free menthol. It is used medicinally and in sun-tan preparations.

Isobornyl salicylate, $HOC_6H_4COOC_{10}H_{17}$, is an oily liquid soluble in alcohol, ether or oils. **Bornyl salicylate** is an isomer. The two esters are used as perfume fixatives, and the iso compound in sun-tan preparations as a fluorescent compound which alters the wave length of light passing through it.

Methyl cinnamate, $C_6H_5CH:CHCOOCH_3$, is a colorless crystalline compound, soluble in ether and very soluble in alcohol. It has an odor resembling that of strawberries and is used in flavoring materials and perfumes, particularly as a soap perfume.

Ethyl cinnamate, $C_6H_5CH:CHCOOC_2H_5$, is a colorless, oily liquid soluble in alcohol and very soluble in ether. It has an odor resembling that of cinnamon and is used in flavoring extracts and perfumes.

Benzyl cinnamate, $C_6H_5CH:CHCOOCH_2C_6H_5$, is a white, crystalline ester, soluble in alcohol or ether. It has a pine-like tone and is used as an odorant and fixative.

Methyl anthranilate, $H_2NC_6H_4COOCH_3$, is a colorless, crystalline compound, slightly soluble in water and very soluble in alcohol or ether. It turns yellow on exposure to sunlight. This ester is prepared synthetically and occurs in many natural essential oils. The material has an odor variously described as like that of orange flowers or of grapes. It is sometimes called **artificial oil of neroli.** The ester is used in orange-flower, gardenia and honeysuckle perfumes and in artificial strawberry and grape flavors. **Dimethylanthranilate,** $CH_3NHC_6H_4$-$COOCH_3$, is similar in properties and uses. It is much more expensive but does not discolor as readily. **Ethyl anthranilate,** $H_2N_2C_6H_4COOC_2H_5$, is similar to the methyl ester and similarly used, but has a more delicate odor and is more expensive.

Dimethyl phthalate, $C_6H_4(COOCH_3)_2$, is a colorless liquid miscible with alcohol or ether, prepared by the esterification reaction of phthalic anhydride and methyl alcohol. It is used as a plasticizer in nitrocellulose and cellulose acetate lacquers, in celluloid to replace camphor, and in perfumes. **Diethyl phthalate,** $C_6H_4(COOC_2H_5)_2$, is similar to the methyl derivative in properties and uses. In addition it is used as a denaturant for alcohol and for oiling textiles. **Dibutyl phthalate,** $C_6H_4(COOC_4H_9)_2$, is similar to the methyl and ethyl compounds in properties and uses. It is also used as a lubricant. **Dibutoxyethyl phthalate,** $C_6H_4(COOC_2H_4OC_4H_9)_2$, is both an ester and an ether. It is a plasticizer for nitrocellulose and some plastics. **Diamyl phthalate,** $C_6H_4(COOC_5H_{11})_2$, is similar to the other dialkyl phthalates in properties and uses. **Glycol phthalate,** $C_6H_4(COOCH_2)_2$, is a yellow to brown liquid soluble in absolute alcohol and in petroleum ether. It is used for purposes similar to those of the dialkyl phthalates. There is also a **glyceryl phthalate** which is similar.

Triphenyl phosphate, $(C_6H_5)_3PO_4$, is a colorless crystalline compound insoluble in water but moderately soluble in alcohol or ether. It is a derivative of phenol prepared by boiling phenol and phosphorus oxychloride in the presence of zinc chloride, treating with alkali, filtering and dissolving the residue in ether. Water is removed from the ethereal solution with anhydrous calcium sulfate, and after filtration, the ether is evaporated off. It is used as a noncombustible camphor substitute in making celluloid, for fireproofing and stabilizing cellulose esters and airplane dope, for impregnating roofing paper, and as a lubricant and plasticizer in various products.

Tricresyl phosphate, $(C_7H_8)_3PO_4$, is commercially a mixture of the product obtained by treating mixed cresols with phosphorus oxychloride as described for making triphenyl phosphate. It is a white to yellow liquid insoluble in water but very soluble in alcohol or ether. Quoted types are C.P. and grades 1 and 2 of technical material, differing in quality and price. It is used as an important plasticizer in cellulose ester lacquers and plastics.

Sulfonmethane or **sulfonal,** $(CH_3)_2C(SO_2C_2H_5)_2$, is a colorless crystalline compound slightly soluble in cold water, moderately soluble in hot, very soluble in absolute alcohol and slightly soluble in ether. It is prepared from anhydrous acetone and ethylmercaptan by reaction in anhydrous hydrochloric acid. The mercaptole formed is oxidized to give sulfonmethane. The latter is used in medicine as a hypnotic and sedative.

Sulfonethylmethane, trional or **methylsulfonal,** $CH_3C(SO_2C_2H_5)_2C_2H_5$, is a white crystalline compound prepared by passing anhydrous hydrogen chloride into a mixture of anhydrous ethyl mercaptan and methyl ethyl ketone, and oxidizing the resulting product. It has solubilities similar to those of sulfonal and is used in medicine as a hypnotic and sedative. Trional is a U.S.P. preparation melting between 74° and 76°C.

CHAPTER XXV

FATS AND FATTY OILS

Doubtless many of us think of fats and oils as just another form of food, but due to their wide distribution throughout the animal and vegetable kingdom, there are many forms and they serve many purposes. In solid form this type of material is usually called fat, and in liquid form oil, although with this classification the same substance might well be a fat in one country and an oil in another, according to the climate. Actually there is no sharp distinction between fatty oils and fats. Therefore the terms are somewhat interchangeable. In plants, fats and oils are largely stored in the seeds and fruits; in animals, in the cellular tissues of the intestines and back, and in the liver.

Essentially, the chemical composition of fats and fatty oils is that of an ester formed by the union of glycerine with three molecules of fatty acids, although when isolated from natural sources, their composition is never limited to that of a single chemical compound. On the hydrolysis of fat, glycerine and fatty acids are therefore liberated. A naturally occurring oil or fat consists of glycerides in which saturated or unsaturated fatty acids may predominate, or fatty acids with longer or shorter carbon chains. The majority of glycerides in turn are themselves mixtures; for example, dipalmito-stearin, in which one molecule of glycerine is combined with two molecules of palmitic acid and one of stearic acid; or palmito-oleo-stearin, in which three different fatty acids are combined with one molecule of glycerine. Although olive oil contains about 75 per cent of oleic and 8 per cent of linoleic acid, about 60 per cent is in the form of mixed oleo-linoleic glycerides.

Commercial fats contain a small percentage of material other than glycerides. This consists of coloring matter, albuminoids, resinous substances and sterols. These are all grouped together under the heading "unsaponifiable matter." The amount present is usually 1 to 2 per cent. The sterols differ chemically according to the origin of the fat. Phytosterol is characteristic of fats of vegetable origin, while cholesterol is characteristic of fats of animal origin. This furnishes a means of differentiating the general source of fats and oils. The fatty-acid content of fats and oils is frequently mentioned in the literature as meaning fatty acids present as glycerides rather than as free fatty acids.

Before the World War, fats and oils could be classified fairly distinctly between edible and industrial types. During the war, fats were at a premium, not only because of their food value, but also because of the glycerine which went into explosives. As fats became more and more scarce, new methods of refining and purification were developed. As a result practically all fats can be used today as a food, except the few like castor and chaulmoogra oils which have definite physiological effects. Whether an oil is used industrially or as a food depends largely on the degree and method of purification. The U.S. Food and Drug Administration defines **edible fats** and **edible oils** as "such glycerides of the fatty acids as are recognized to be wholesome foods. They are dry, and sweet in flavor and odor."

Material which is very high in fatty matter can be rendered, that is, boiled up with water. Rendering is applied in the production of tallow, lard, bone fat, whale oil, palm oil and the best grade of coconut oil. The fatty matter is cut up into small fragments, transferred to vessels containing water and heated by steam, sometimes under pressure. The cell structure is broken up, the melted fat flows out as an oil and forms a layer on top of the water, while the membranous material settles to the bottom. The oil is drawn off and filtered. Residual matter is usually pressed to yield more oil.

Small nuts and seeds cannot easily be rendered. They are freed from sand and other impurities, the shells and husks removed, and the kernels converted into meal by grinding. To obtain oil for industrial purposes, the meal is heated and then pressed. For the preparation of edible oils, the meal may be packed in bags and subjected to hydraulic pressure in the cold. Cold-pressed oil has less color and contains fewer impurities than oil previously heated. However, the oil extraction is incomplete by this method. More oil is obtained by pressing the same meal at a somewhat elevated temperature. Seeds low in oil are always heated before pressing. Various grades of oil are obtained according to the care of the manufacturer and the temperature of the extraction process. Residual meal is used for cattle food or fertilizer.

Even after the above treatment the cakes may contain as much as 10 per cent of oil. If it is desired to obtain this, extraction with volatile solvents is resorted to. Carbon bisulfide has been used over a long period for this purpose. Some more modern equipment uses petroleum ether for extraction, applying types which can be recovered with very little left in the oil. Solvent extraction is carried out both cold and hot. It may be applied to oil cake or to a coarse fresh meal. The treatment depends on the type of material being extracted and the purpose for which the product is to be used.

Fats such as tallow are often subjected to pressure to squeeze out the liquid or "oleo" portion and leave the "stearin." The latter may separate from salad oils at low temperatures, so that such oils are usually treated to remove it. Oils may be chilled, for example to 12°C. in the case of cottonseed oil, to separate out the portion which would solidify at low temperatures. The solid part, called **vegetable stearin,** is then filtered off. The liquid portion or filtrate is known as **winter oil** because it will remain unchanged in winter weather, that is at low temperatures. Oil which has not been so treated is called **summer oil.** Summer oil may precipitate out solids, illustrated by the occasional clouding of salad oil when kept in a refrigerator. To improve the color of oils and fats, they may be filtered through adsorbents such as diatomaceous earth, activated carbon, etc.

Free fatty acids in oils and fats, for most purposes, are considered contaminating agents, so that the purity of a product is often defined by giving both color and free fatty acid content. For example, peanut oil imported from the Orient is described as edible when it contains less than 2 per cent of free fatty acids and has a light yellow color. Prime yellow peanut oil must not contain more than 0.2 per cent of free fatty acids, while choice refined must not contain more than 0.1 per cent. Many of our edible oils actually contain less than 0.05 per cent of free fatty acids.

Probably the best known method of purification is to heat the fat, if necessary, to liquefy it. To the liquid is added a sufficient amount of aqueous solution of caustic soda to react with the free fatty acid, converting it to soap. Because of the small amount of water present, this soap is insoluble and therefore the filtration of the oil through fullers' earth or other adsorbents removes the soap as well as color and odorous contaminants. Free fatty acid content is therefore in general indicative of the degree of refinement, rather than characterizing an individual fat or oil. Much color, high fatty acid content and the presence of extraneous matter, mark a low degree of refining.

Some oils are blown with air to remove undesirable odors and brighten them. When carried out to any substantial extent, particularly with drying oils, this thickens them and they are known as **blown oils.** There are numerous other methods of treatment, bleaching with hypochlorites, bleaching with potassium bichromate and sulfuric acid applied particularly to palm oil, etc.

One method of preparing lard combines rendering and refining in one operation and is said to yield a high-grade lard. Vacuum protects the lard from contact with air during the whole process. Continuous extraction of an oil-bearing mass by a solvent, applying the counter-current principle is carried out in various types of structures. A continuous method for refining oil with lye is in use. In other processes, oils are refined with phosphoric acid. Another treatment is with boric acid at temperatures above 100°C., followed by distillation. Liquid ammonia and alkylolamines are used for refining fats, oils and waxes. Fish oils are decolorized and deodorized by polymerization at 200-300°C. under reduced pressure. Oils may be treated with peroxides at temperatures below 75°C. to improve subsequent bleaching by adsorbents.

The demand for hard fats is such that oils are frequently hardened by hydrogenation, that is, unsaturated bonds are changed to saturated bonds by the addition of hydrogen. This is accomplished by passing hydrogen gas through the oil, which is intimately mixed with a metallic catalyst such as nickel, nickel-aluminum alloy, etc. The process is carried out at an elevated temperature. Much work has been done to evolve new and efficient catalysts. The hydrogenated oil is filtered hot to free it from the catalyst and the latter recovered.

Fats and oils are frequently classified according to their capacity for absorbing iodine. Those with a high capacity for absorbing iodine, that is, with a high proportion of double bonds, are called **drying oils**; those intermediate in capacity are called **semidrying,** and those of low capacity, **nondrying.** Solid animal fats are nondrying. In general the nondrying and semidrying oils are used as foods and as lubricants and the drying oils as paint and varnish ingredients. Drying oils gradually become oxidized on exposure to air by taking up oxygen at the double bonds. Either may be used as soap stock according to the market, but the nondrying oils are preferable because they impart less odor to the soap produced.

The classification followed below is a combination based on both character and source. It would be impossible to include all the known fats and oils. The intention is to list the more important commercial products. Similarly it is impossible to include all of the uses of an oil. The more important ones are mentioned. The physical constants are mentioned in the context only when explanatory of a special use.

As a convenient classification, fats and oils are listed under headings of animal fats and oils, vegetable fats and oils, and fish oils, with a supplementary class of fish-liver oils. Roughly they are given in order of decreasing melting point. This brings closely related fats and oils near each other.

Fats and oils are insoluble in water, soluble in ethyl ether, petroleum ether, carbon bisulfide, carbon tetrachloride, chloroform, benzene and naphtha. They are slightly soluble in alcohol, except for castor oil, which is readily soluble. Castor oil also dissolves in acetic acid. Fats and oils mix with each other and with mineral oils, with the exception of castor oil which is immiscible with mineral oils. Specific solubilities of individual oils are therefore unnecessary.

Oils and fats are characterized by chemical and physical constants, the more common being shown in the tables at the end of this chapter. This avoids much detailed description with each oil. The **melting point of fats** is the temperature at which they melt as the temperature is raised gradually, not necessarily the same as the solidifying point. The **specific gravity of fats** is the ratio of the weight of a definite volume to the weight of the same volume of water. The **saponification value of fats** is the number of milligrams of potassium hydroxide necessary to saponify completely one gram of the fat or oil. The **iodine value of fats** is the percentage of iodine with which the sample reacts under standard conditions. The **refractive index** measures the refraction of monochromatic light when passing from air into the oil or fat. The percentage of **unsaponifiable matter** in fats is the percentage of matter present which is incapable of saponification. Specific gravity and refractive index are referred to a definite temperature, since the values vary with temperature. For more complete tables of constants consult a standard chemical handbook.

Fatty acids of many types, which are closely related to the oils used as soap stocks, have been discussed in their proper chemical classification under organic acids. These include related products such as rosin oil and tall oil of somewhat doubtful classification, placed there because they are not fatty acid glycerides as are all fats and fatty oils.

Animal Fats and Oils

Tallow or **animal tallow** is a general name which usually refers to **beef tallow** but which may also include **mutton tallow** and **horse fat,** since the chemical and physical properties of the fats from the three sources are closely related. Grading other than edible, is by the quality of the tallow rather than by source, and will be discussed more specifically under beef tallow. In general the classifications are that the highest and most expensive type is "acidless," with "edible" grade second and "extra" a third grade. Lower grades represent less refinement.

Beef tallow is a white to yellow solid and consists mainly of stearin, palmitin and olein, containing about two-thirds of the first two and one-third olein. It is obtained from beef fat by pressing out as much olein as possible. The edible grade of beef tallow is used as shortening in food products. Lower grades are extra, city extra and special. Tallow is also used for the manufacture of stearic acid, for the manufacture of leather dressings, and in various lubricating compositions. Soap is made from tallow, often from grades derived from **house grease.** This is a fat derived from rendering fatty garbage. It is usually dark brown in color because the fatty matter is so often scorched in cooking.

Stearin or **oleostearin** is a white solid prepared from first-run tallow by submitting it to hydraulic pressure. A liquid fraction is squeezed out, leaving the solid stearin lower in olein than is tallow. Stearin consists largely of the glyceryl ester of stearic acid. A technical grade is sold for use in soap, for impregnating fabrics, as a textile size and for water-proofing materials. Stearin is also used in margarine.

Mutton tallow, derived from sheep's fat, has much the same appearance and composition as beef tallow, contains slightly less of the liquid fat, olein, and is a little harder. It is put to the same uses as beef tallow, but is less desirable because of its greater tendency to turn rancid.

Lard is a white fat obtained from hogs and is somewhat softer than tallow. It contains about 40 per cent of palmitin and stearin and 60 per cent of olein. **Leaf lard** No. 1 is obtained from the fat around the intestines and kidneys, and is the best grade. The next grade, neutral lard No. 2, also edible, is obtained from the fat of the back. Inferior qualities are obtained from any part of the animal with the aid of steam. Commercially quoted grades include choice western, city, middle-western, neutral and U.S.P. The U.S.P. grade is defined as the internal fat from the abdomen of the hog, free from rancidity, and melting at 36-42° C. Lard is used in cooking, in making margarine, in the manufacture of soap, in pharmacy as an ingredient of ointments, and in perfumery in the making of pomades. **Lard compound** is a thickened edible cottonseed oil. The use of oleostearin for the purpose has been followed by the use of stearin from other sources, including hydrogenated cottonseed oil and vegetable stearin. **Benzoinated lard** is a U.S.P. product prepared by heating 10 grams of Siam benzoin with 1000 grams of melted lard at 60°C. for two hours and filtering. It may contain 5 per cent of white wax, bleached beeswax.

White grease is a fat very similar to lard in appearance, but inedible. It is the fat obtained from the kidneys and back of hogs, but which is too high in fatty acid content, or is objectionable in some other way for use in food. **Yellow grease** is the fat obtained from the parts of the hog remaining after those parts yielding white grease are separated. It is inedible and similar to white grease except in color. Both white and yellow greases are used in making soap.

Butter fat is derived from cow's milk which contains on an average about 3.75 per cent of this fat. When the milk is allowed to stand, the fat concentrates in a layer at the top in the form of cream. The cream is skimmed off and churned to separate the yellow butter fat. This fat differs from other natural animal fats in that it contains the glycerides of water-soluble fatty acids in considerable amounts, butyric, caproic, caprylic and capric acids, in addition to the higher fatty acids. The Reichert-Meissl value which measures the relative amount of volatile acids is very high as compared with that of other fats, 24-34. Butter fat is the main constituent of **butter,** which contains about 81 per cent of fat, 15.5 per cent of water, 2.7 per cent of salt and 0.8 per cent of casein and ash. Butter has a naturally deep color when produced from milk in the summer months, particularly in June when grass is high in chlorophyll. Therefore for the balance of the year the color of "June butter" is taken as a standard and that color equaled or exceeded by the addition of a mixture of bixin and curcumin. The former is a vegetable dye derived from the fruit of the annatto tree and the latter from turmeric. Certified food colors are also permitted in nearly all states. The artificial coloring of butter is so universal as to be exempted from declaration of artificial color under the Food and Drug Act. Butter fat is one of the important sources of vitamin A in the diet.

Margarine or **oleomargarine** is a fat product deserving of mention because of its commercial importance. Margarine may be made from animal fats, from vegetable fats and oils, or from a mixture of these. The basis of **animal margarine** is oleo oil, the liquid fraction which separates from a hard fat when tallow is pressed. **Vegetable margarine** is usually composed of a hard fat mixed with a liquid oil. The hard fat portion may be 25 per cent of hydrogenated oil or 65 to 70 per cent of coconut or palm kernel oil. Many liquid oils are used, including cottonseed, peanut, soybean, etc. In mixed margarine either first-run tallow or stearin may be combined with highly purified liquid vegetable oils. The fat charge is churned or emulsified with milk, which has been soured under controlled conditions, to give the product a butter flavor. Annatto or other coloring matter may be added and in some cases a vitamin concentrate is added so that the margarine will have the same nutritional value as butter. In the United States these additions are restricted by high taxation. In some countries it is required by law that a harmless substance be added to margarine so that it can be distinguished readily from butter. This is usually sesame oil.

Levies on foreign oils imported into the United States vary from time to time and bring about corresponding variations in prices and in the production of domestic oils. Several states have levied state taxes on margarine containing oil or fat not of domestic production. This resulted in increasing the use of cottonseed oil as well as beef oleostearin, and decreasing the use of coconut oil in margarine, in these localities. In the early part of 1935 only 16 per cent of the margarine produced in the United States contained mixed animal and vegetable oils, the other 84 per cent was made from vegetable and nut oils.

Degras or **wool grease** is a crude dark-colored grease obtained in the process of degreasing sheep's wool. Some grades contain fatty acids derived from the soap used in wool washing. This leads to the quotation of common degras and neutral degras. Both are available in domestic and English grades at competitive prices. Degras is used in printing inks, in special soaps, in leather dressing and for the production of lanolin. A fatty substance obtained by the action of oxidized fish oil in chamoising leather is also called degras, usually moellons or moellons degras.

Lanolin, lanum or **refined wool fat** is a brownish yellow to nearly white unctuous grease obtained by purifying wool grease. It is more closely related to waxes than to fats because it contains a major portion of cholesterol esters of fatty acids instead of glyceryl esters. Technical and U.S.P. grades are sold, both hydrous, *adeps lanae hydrosus*, and anhydrous, *adeps lanae*. U.S.P. hydrous lanolin contains 25-30 per cent of water; the anhydrous melts at 38-42°C. Lanolin has the property of taking up a large amount of water to form a stable emulsion. The better grades are used as an ointment base, a superfatting agent for toilet soaps, and very widely in cosmetic creams. Lanolin is one of the few fats absorbed by the skin and therefore finds use in skin-softening, sunburn and "skin food" preparations. Poorer grades are used in leather dressing as a finishing and softening agent.

Oleo oil is a yellow liquid obtained by cold-pressing first-run tallow, that is, the tallow obtained in the first rendering process. The liquid portion is separated by hydraulic presses and consists mostly of olein, with a small amount of palmitin included. Grades are No. 1 and No. 2. Another grade is known as acidless oleo oil or acidless **tallow oil.** Various grades of oleo oil are used in making margarine and soap, and as a lubricant base.

Lard oil is a colorless to yellow liquid obtained by cold-pressing lard, the same as oleo oil is obtained from tallow. The chief constituent is olein, with a small percentage of the glycerides of higher fatty acids. There are numerous grades such as common no. 1, common no. 2, extra, extra no. 1, headlight burning, prime edible, prime inedible, winter prime and winter strained. Cottonseed oil or petroleum oil are sometimes used to adulterate inedible grades. Uses are varied, for food manufacture, for burning for special purposes, etc. Large amounts are used in metal-cutting compounds and for oiling wool. It is too expensive for use as soap stock.

Neatsfoot oil, bubulum or **hoofoil** is a pale yellow oil obtained from the shin bones and feet, not hoofs, of cattle. It usually contains only a relatively small portion of oil derived from horses. It is sometimes sold according to the temperature at which stearin separates, that is, 20°, 30° and 40°F. Other designations are cold test, extra, extra no. 1, pure and special. Its uses are as a lubricant for delicate machine parts, for oiling wool, and for high-grade leather dressing. It is an expensive oil and is sometimes adulterated with corn, rapeseed, cottonseed, fish, or mineral oil.

Seal oil varies in color from brown to colorless. The oil is graded according to color, the poorest being darkest, brown, yellow, straw and water-white. Its use is for soap manufacture and leather dressing.

Bone fat or **bone oil** is obtained from the bones of animals by rendering them with hot water or steam, or extracting with an organic solvent. It is used in making soap and in pharmacy for the preparation of pomades.

Whale oil, train oil, body oil or **blubber oil** is a yellow to brown oil with a fishy odor, obtained by boiling up the blubber or protective layer of fat which lies just under the skin of the whale. The oil is graded as crude no. 1, crude no. 2, natural winter, bleached winter and natural refined. It is frequently sold on the basis of its free fatty acid content, or with a maximum acid-content guarantee. It is used in soap, for lubrication, illumination, leather dressing, and tempering steel. After refining and hardening by catalytic hydrogenation, it may be deodorized for use in food products such as margarine.

Porpoise jaw oil is light yellow. Its chief use is as a lubricant for watches and other delicate instruments made of steel. Its value lies in its noncorrosion of metal and freedom from any tendency to gum or thicken, even at low temperatures. It is extremely expensive. **Porpoise body oil** or **dolphin oil** is also pale yellow. It is used as a lubricant for fine machinery and as a leather dressing.

Turtle oil is a yellow semisolid oil obtained from the eggs and the body fat of turtles. Like cod-liver oil it is valued for its high vitamin A and D content. Some is used in cosmetics. The price is high.

Egg yolks are the yolks of hens' eggs obtained after separating the whites. The yolks are mixed with salt or sugar, and sometimes with borax as a preservative, and enter the market as a yellow to orange semisolid. Domestic and imported grades are quoted. They are high in fats, and are used in baking for their food value, as an emulsifying agent and fatty constituent in pharmaceuticals, in leather dressing and as a tawing agent on skins. **Frozen egg yolks** are also sold.

VEGETABLE FATS AND OILS

Cocoa butter, cacao butter or **oil of theobroma** is yellowish, hard and brittle. Since it is separated from chocolate it has a chocolate odor and taste. The U.S. Food and Drug Administration defines edible cocoa butter as the edible fat obtained from sound cacao beans (seeds of *Theobroma cacao* or other closely related species), either before or after roasting. The main ingredients are glycerides of stearic, palmitic and lauric acids. It is sold as crude and refined. While the latter is quoted in quantities as lumps, it is formed into cakes for minor sales. It is also sold as a U.S.P. product melting at 30-35°C., which must be from the roasted cacao. Cocoa butter is used in pharmacy in ointments and suppositories, for coating pills and in some cosmetics. It is also used in confectionery in conjunction with chocolate which requires additional cocoa butter. The use of other fats for this purpose is not permitted. Cocoa butter is relatively expensive and therefore does not compete in a general way with other fats and oils for edible or industrial purposes.

Japan wax, Japan tallow or **sumac wax** is chemically not a wax but a glyceride. This wax-like fat comes from the fruit of a Japanese sumac tree. It consists mostly of glyceryl palmitate with 4-12 per cent of palmitic acid. Japan wax is used in making candles, and as a substitute for beeswax in polishes. It is fairly expensive and therefore not used as soapstock.

Bayberry wax is a wax-like fat consisting largely of the glycerides of palmitic, myristic and lauric acids. It is obtained by boiling the berries of the bayberry or wax-myrtle shrub, when the wax on the berries melts and floats to the surface where it can be collected. The green, rather brittle, solid fat is imported and used in making candles for the pleasant odor it gives when burned.

Palm oil or **palm butter** is reddish yellow and contains glycerides of palmitic, stearic and oleic acids. The fresh oil has a violet-like odor. Commercially it often has the odor of fatty acids from rancidity. It is obtained from the fermented pulp of the fruit of the palm tree, *Elaeis guineensis,* grown in South America and West Africa. Niger and Sumatra grades are quoted. The "soft" oils of commerce are those low in free fatty acids, the "hard" oils, those high in free fatty acids. The crude oil develops free fatty acids with great rapidity. Soft oil is quoted as 12½ and 20 per cent, meaning content of free fatty acids calculated as palmitic. Palm oil is used in the manufacture of soap and candles, as a lubricant, as a rubber softener, and in the tin-plate industry. For soap making, the naturally orange-colored oil is bleached by oxidation, either chemically or by air.

Chinese vegetable tallow is a white amorphous fat derived from the fruit of the Chinese tallow tree. It is used for making soaps and candles, and as a lubricant. The supplies and price are highly variable. Some is used in making kosher soap. **Shea butter** is somewhat similar and is obtained from the seeds of the shea tree. **Borneo tallow** is similarly derived from several species of trees.

Ti-tree oil is an expensive oil from any of a series of Asiatic and Polynesian palms and shrubs. It is used only in a limited way for medicinal purposes.

Cottonseed oil is yellow or red to brown, is semidrying in type and is obtained from the seeds of the cotton plant. Grades are crude, refined, prime summer yellow, bleachable and U.S.P. Brazilian, crude, British semirefined and PCY grades are also quoted. Crude oil containing not more than 2 per cent of fatty acids is refined to give edible oil. Other classifications are domestic cooking and domestic salad grades. The U. S. Food and Drug Administration defines the edible grade as the edible oil obtained from the seed of the cotton plant, *Gossypium herbaceum L.* or from the seed of other species of Gossypium. **Cottonseed stearin,** the solid portion which separates out on chilling the original oil, consists largely of palmitin and is used in making margarine, lard compounds, soap, and as a textile size. The hydrogenated oil is used as a lard substitute, and the oil itself as a salad and cooking oil. It is a major food oil. Cottonseed oil is also used in soap and cosmetic cream production, as a leather dressing and a lubricant. The U.S.P. grade of **camphorated oil** contains 20 per cent of powdered camphor in 80 per cent of cottonseed oil.

Tung Oil, Chinawood Oil, Japanese Wood Oil or **Wood Oil** is a brown to yellow drying oil, varying in color according to whether the seeds of the tung tree are expressed hot or cold. The dark grades of the oil are characterized by a very strong unpleasant odor. It has the highest specific gravity, 0.936-0.943, of the fatty oils except for castor oil. A characteristic property of Chinawood oil is the readiness with which it polymerizes. It sets to a hard jelly when heated for a short time to 250° C. It also solidifies due to polymerization when a saturated solution of iodine is allowed to come in contact with the surface of the oil. Tung trees have been planted in Florida and are successfully grown there. They are also cultivated in several parts of the British Empire, some South American countries, and Russia, in an attempt by the various countries to have independent supplies of this raw material. Commercial grades of the oil are white, yellow, dark and black. Japanese tung oil is inferior to the Chinese oil and has poorer drying qualities. The oil is used for waterproofing and in protective coatings. It has been essential to some types of varnishes. Because of its derivation from a natural source, and supply largely by importation, it is subject to wide fluctuations in price. The American crop is increasing yearly.

Oiticica nut oil is a drying oil much resembling tung oil in properties. This oil from Brazil replaces tung oil to some extent in the manufacture of varnish. It is of sufficient importance so that futures are quoted. The production is being expanded rather rapidly.

Peanut oil, groundnut oil, earthnut oil, arachis oil or **Katchung oil** is a yellow to green, nondrying oil obtained by pressing or extracting ground peanut meats. Glycerides of arachidic acid give it its characteristic taste. Other high molecular-weight acids are also present as esters. The edible grade is defined by the U.S. Food and Drug Administration as the edible oil obtained from the peanut, *Arachis Hypogaea.* Many grades are quoted, including domestic crude and edible refined. Many distinctions in the refined oil are a matter of free fatty acid content, varying from 0.1 per cent of free fatty acids for choice refined, to 0.25 per cent of free fatty acids for good-off refined, according to the standards of the New York Produce Exchange. Peanut oil is used widely abroad as a salad oil and in making soap. It serves the same purposes in the United States but is less important. This oil also appears as a substitute for olive oil.

Sesame oil, benne oil, teal oil or **gingily oil** is a yellow semidrying oil expressed from the seeds of a plant commonly grown in the Far East. Commercial grades are yellow and white. It is edible when sufficiently low in free fatty acid content. The edible grade is defined by the U.S. Food and Drug Administration as the edible oil obtained from the seed of the sesame plant, *Sesamum orientale, Sesamum indicum,* or *Sesamum radiatum.* Other grades are semirefined and coast. It is used in margarine, in soap and cosmetics, and in general where olive and almond oils are used, and may be an adulterant in these. Some countries require the inclusion of a small amount of sesame oil in margarine, as the oil gives a color reaction which could then be used to distinguish margarine from butter.

Soybean oil, soya bean oil, Chinese bean oil, soja bean oil or **soy oil** is a pale yellow semidrying oil. The soybean plant is cultivated very extensively in Asia and to a rapidly increasing extent in the United States. The oil contains mostly olein and linolein. The U.S. Food and Drug Administration defines the edible grade as the edible oil obtained from the seed of various varieties of the soybean plant such as *Glycine soja.* Grades are crude, refined and coast. The oil is used as an edible oil, in soap manufacture, in inks, paints and varnishes and when suitably processed serves as a substitute for linseed oil. Resinous materials have been produced from it. Fermented soybean oil is an important condiment in the oriental diet.

Palm-kernel oil or **palm-nut oil** is obtained from the nut of the same species of palm which furnishes palm oil. It has a yellowish color and contains the glycerides of a wide range of fatty acids from caproic to stearic. It is closely related to coconut oil. Crude and refined grades are available. The U.S. Food and Drug Administration defines the edible grade as the edible oil obtained from the kernels of the fruit of the palm tree, *Elaeis guineensis* or *Elaeis melanococca.* It is used both as an edible oil and as a soap fat.

Coconut oil or **cocoanut oil** is a liquid in the tropics and a white solid in temperate climates. Occasionally therefore it is referred to as **coconut butter.** It is obtained from the fruit of the coconut palm and is extracted from the coconut meat by various methods. The content of unsaturated fatty acids is very low. Coconut oil contains a high proportion of the lower saturated fatty acids such as lauric and myristic, and some of the more volatile acids including capric and caprylic. Being an imported fat it is taxed. Grades are designated by the localities where they are produced, mainly Ceylon, Manila and Cochin. The latter is considered the best. An edible grade melting at 76°F. is quoted, as well as futures, usually for 3 months ahead. The edible oil is defined by the U.S. Food and Drug Administration as that obtained from the kernels of the coconut, *Cocos nucifera* or *Cocos butyracea.* Coconut oil is used in large amounts as a soap fat to give lather to white soaps. It is the fat used to make hard-water soaps and usually kosher soaps. The major part of liquid soaps and liquid shampoos are made from it. The refined grade is used in margarine and to a lesser extent in cosmetics.

Copra oil is a light-colored, semisolid oil obtained by expressing the dried kernels of coconuts. It has about the same constants and may be considered as an inferior grade of coconut oil. Copra oil is used in making candles and soap. Sometimes the term is used synonymously with coconut oil.

Babassu oil is a solid, creamy-white fat obtained from the nut of a Brazilian palm. It greatly resembles coconut oil in consistency and in general characteristics, and is used in the manufacture of soap.

Olive oil, sweet oil, Florence oil or **Luccu oil** is a yellow to green, nondrying oil derived from the fruit of the olive tree. Various grades are obtained by cold-pressing, hot-pressing, and extracting with solvents. The first cold-pressed oil is called virgin oil, is very light in color and constitutes the best grade. The same oil cake may be pressed a second and a third time, pressed hot and finally extracted with solvents. In California low-grade oil is improved by washing with water and carbon dioxide vapor, or by treatment with steam *in vacuo*. That extracted with carbon bisulfide is known as **sulfur oil** or **olive-oil foots.** The chief constituents of olive oil are olein and palmitin.

According to the standards of the New York Produce Exchange, the edible oil should not contain over 1.5 per cent of free fatty acids. The U.S. Food and Drug Administration defines the edible grade as the edible oil obtained from the sound mature fruit of the olive tree, *Olea europæa.* The commercial grade is much the same as the edible grade except that the flavor is not as good and the fatty acid content may be as high as 7 per cent. A U.S.P. grade is also prepared. Olive oil foots are green and may have a free fatty acid content ranging from 20 to 50 per cent. Olive oil is relatively expensive and is sometimes adulterated with such oils as cottonseed, peanut, sesame and poppy. **Denatured olive oil** contains oil of rosemary, which makes it inedible and permits its import at a lower tax rate. Olive oil is used as a food, in ointments and cosmetics, for Castile soap manufacture, as a lubricant, a wool oil, and in tanning. The olive-oil foots are a soap stock and produce a characteristic **green bar soap,** often imitated by the coloring of other soaps of low-titer oils.

Teaseed oil or **tea oil** is a straw-colored, nondrying oil resembling olive oil. It is obtained from the seeds of a Chinese tree related to, but not the same as the shrub which yields tea leaves, and is sold as crude and refined. The oil is used for food, in soap making, as a lubricant and as a substitute for olive oil in sulfonated grades.

Sunflower oil is a pale yellow drying oil expressed from sunflower seeds. The U.S. Food and Drug Administration defines the edible grade as the edible oil obtained from the seed of the sunflower, *Helianthus annuus.* Crude and refined grades are sold. It is used as an edible oil, in varnishes and in soap.

Poppyseed oil or **poppy oil** is colorless to yellow or red, and is obtained from the seeds of the opium poppy. It is a drying oil. The U.S. Food and Drug Administration defines the edible grade as the edible oil obtained from the seeds of the poppy, *Papaver somniferum.* Grades are crude, red and white. The white or cold-pressed oil is used as a salad oil, for artists' colors and in varnishes. The dark or hot-pressed oil is used for making soft soap and in paints.

Linseed oil is obtained from the seeds of the common flax, and varies in color from yellow to brown. It is a valuable drying oil characterized by its unusually high content of the glycerides of unsaturated fatty acids, including oleic, linoleic, linolenic, and isolinolenic acids. There is a U.S.P. grade of raw linseed oil, as well as the technical grades. It is used very extensively in making paint, varnish, printing and lithographic inks, linoleum and soft soap. **Boiled linseed oil** is largely used in paints. Grades are boiled and double boiled. This terminology means that it has been heated and blown with air to oxidize it, rather than being boiled. Color is an important factor in the many grades available.

Sulphurated linseed oil is a solution of elementary sulfur in linseed oil, prepared by heating the two together. It is a thick, brownish red liquid, used as an antiseptic.

Factice or **rubber substitute** is a rubber-like solid produced by heating an unsaturated oil with sulfur or sulfur monochloride. Linseed and rapeseed oil are typical of the oils used. Factice is also known as **vulcanized oil.** Grades vary from white through brown to black, and are semitranslucent.

The material is used in compounding rubber and as a substitute for rubber in some products.

Perilla oil is a light yellow drying oil obtained from the seeds of a form of mint grown commonly in Japan and East India. It has the highest iodine value of any known oil. It resembles linseed oil in odor and taste but is inferior in drying quality, and has a tendency to form drops rather than a film when spread on a smooth surface. Technical grades are sold. It is sometimes adulterated with cottonseed oil. In the far East it is used as an edible oil. Other uses are in the manufacture of varnishes, artificial leather, inks, etc.

Rapeseed oil, rape oil or **colza oil** is a yellow to brown semidrying oil obtained from the seeds of a plant resembling the cabbage. The edible grade is defined by the U.S. Food and Drug Administration as the edible oil obtained from the seed of the rape plant, *Brassica napus,* or from the seed of closely related Brassica species which yield oils similar in composition and character. It is sold as crude and refined or water-white. A denatured grade is also sold. It is used as food, as a lubricant, in rubber substitutes and in the heat treatment of steel. **Blown rapeseed oil** was much used at one time as a plasticizer in lacquer but has been largely replaced by other substances.

Corn oil or **maize oil** is a pale yellow, semidrying oil obtained from the germ of the kernel of Indian corn. The U.S. Food and Drug Administration defines the edible grade as the edible oil obtained from the germ of Indian corn, or maize, *Zea mays.* It is used mainly as a food oil, either in the original form as a salad oil or after hydrogenation as a solid shortening.

Hempseed oil or **hemp oil** is a light green drying oil which turns yellow on standing. It is obtained from the seed of hemp, *Cannabis sativa.* Crude and refined grades are sold. The oil resembles linseed oil and is used in paints and varnishes, and in soft soap.

Croton oil or **tiglium oil** is a yellow to brown, semidrying oil expressed from the seeds of a tree which grows in southeastern Asia and China. It contains olein and glycerides of the saturated fatty acids from lauric to stearic. Grades are technical, and U.S.P. Its use is in medicine as a powerful purgative.

Walnut oil is a yellow to greenish oil obtained from the nut of the English walnut tree, *Juglans regia.* Crude and refined grades of this oil are sold for use in varnishes and paints.

Sweet almond oil is a yellow, nondrying oil, and consists largely of olein. This is quite different from bitter almond oil which is an essential oil. Technical and U.S.P. grades are sold. It is used in perfumes, cosmetics, as an emollient in pharmacy, and as a lubricant for fine instruments. Because of its relatively high price, it is replaced as far as possible by cheaper oils for use in cosmetics.

Peach-kernel oil is expressed from the kernel of the peach seed. It is yellowish and is used as an inexpensive substitute for almond oil, competing with olive oil for that purpose. It is not to be confused with the essential oil of the same name.

Apricot-kernel oil is a pale yellow, semidrying oil so similar to almond oil that it is used as an adulterant and a substitute for the latter. The domestic and the Russian oils are quoted.

Castor oil or **ricinus oil** is a yellow to brown nondrying oil expressed from the seeds of the semitropical castor-oil plant. It has the highest specific gravity of the known fatty oils, 0.950-0.968. Castor oil is characterized by its high content of ricinolein, the glyceride of an unsaturated hydroxy fatty acid. This gives it the properties of miscibility with alcohol and insolubility in mineral oil. Grades are medicinal, U.S.P., AA, No. 1 and No. 3. The usual industrial grade is No. 3. It is used in medicine for its cathartic action, as a lubricant, especially for airplane engines, a leather preservative, in textile treatment, for fly paper, for sulfonation, in rubber substitutes, in cosmetic creams, hair dressing and in fluid pressure-transmission liquids. **Blown castor oil** is used in polishes, and at one time was used extensively as a plasticizer in lacquers, but has been largely replaced by synthetic products.

Chaulmoogra oil or **gynocardia oil** is a thick, brown to yellow oil or whitish fat obtained from the seeds of an East Indian tree. It consists chiefly of the glycerides of chaulmoogric and hydnocarpic acids. Grades are technical and U.S.P. It is used in medicine in the treatment of leprosy and other skin diseases. The price is not competitive with other fats and oils.

Wheat-germ oil, as the name implies, is a very expensive oil derived from the wheat germ. Its content of vitamin E renders it particularly valuable for administration medicinally, for use in cattle feed to promote lactation, etc.

Iodized oil is a viscous liquid, light in color but turning dark brown on exposure to sunlight. It is produced by treating vegetable oils with iodine. The U.S.P. grade is sold. This contains from 39 to 41 per cent of organically combined iodine. It is used medicinally as a source of iodine.

Fish Oils

Menhaden, mossbunker or **pogy oil** is a brownish drying oil obtained from the body of the menhaden. Classifications are as crude, alkali-refined, blown, kettle-bodied and pressed light. The oil has varied uses, for leather dressing, as a substitute for linseed oil in making patent leather, in paints and linoleum, in printing inks, and when hydrogenated, as a substitute for tallow in soap making.

Sardine oil is a yellow oil obtained by rendering the bodies of sardines and also in the canning of sardines. Grades are crude, alkali-refined, kettle-bodied, pressed light and poultry-feed. It is used in soap when hydrogenated, for leather stuffing, as a lubricant and in poultry food.

Salmon oil is a yellow liquid obtained as a by-product in the salmon-canning industry. The crude oil is used in leather dressing and the refined oil in making soap.

Herring oil is yellow to red and is graded by numbers 1, 2, 2 brown, and winter-pressed. It is used in soap, for currying and finishing leather, and as a lubricant.

Fish-Liver Oils

Cod-liver oil is brown. It contains a fairly large amount of stearin. When freed from stearin, it is known as **"raked" oil.** Commercial grades are dark brown, light brown, pale and U.S.P. The U.S.P. grade contains at least 600 U.S.P. units of vitamin A and at least 85 U.S.P. units of vitamin D per gram. It may contain flavoring substances. There is also a U.S.P. **nondestearinated cod-liver oil** having the same vitamin content as the other but consisting of the whole fixed oil, containing a maximum of 0.5 per cent by volume of water and liver tissue. These edible grades are an important medical source of vitamins A and D. Inferior grades are known as Newfoundland and Norwegian grades of **cod oil** and are used in the dressing of leather and chamois. After it has been used for the tanning of sheep skivers as chamois, it is pressed out and is in an oxidized form known as degras, **moellons** or **moellons degras** used for leather stuffing. When extracted by alkali instead of by pressing, an inferior grade of moellons is obtained known as **sod oil.** Moellons and sod oil have fishy odors as well as those characteristic of rancidity.

Halibut-liver oil or **halibut oil** is yellow to red and is sold in both the crude and refined state. Its concentration of vitamins, particularly A, is several times that of cod-liver oil, which makes it a valuable aid in nutrition. The crude product is used in leather dressing. The edible oil is sold on the basis of its vitamin A concentration expressed in thousand units per gallon. Commercial oils high in vitamin potency are adjusted to the desired standard by dilution with bland U.S.P. vegetable oil, usually cottonseed. Other fish-liver oils which have been found to have a very high vitamin content are **swordfish-liver oil** and certain **tuna-liver oils.**

Shark-liver oil or **shark oil** is a red to brown oil obtained from the livers of several varieties of sharks. Grades are crude and refined. The refined oil is used as a source of vitamins A and D, and the cruder product in the leather industry, and in paint and soap manufacture.

CONSTANTS FOR ANIMAL FATS AND OILS

		Solidifying Point °C.	Specific Gravity Value	Specific Gravity Temp. °C.	Saponification Value	Iodine Value	Refractive Index Value	Refractive Index Temp. °C.	Unsaponifiable Matter, %	
1	Horse fat	20 to 45	0.916–0.922	15.5	195–200	71–86	1.4603–1.4717	40		1
2	Beef tallow	27 to 38	0.943–0.952	15	193–200	35–46	1.4552–1.4587	40		2
3	Stearin, oleo	54 to 56	0.914–0.919	15	193–199	56–60				3
4	Mutton tallow	32 to 41	0.937–0.952	15	192–197	35–46	1.4501	60		4
5	Lard	27 to 30	0.935–0.940	15.5	193–200	50–64	1.4584–1.460	40	0.23	5
6	Butter fat	20 to 23	0.935–0.940	15.5	216–233	26–38	1.459 –1.462	25	0.33–0.56	6
7	Lanolin	38 to 40	0.932–0.945	15	84–127	15–29	1.4781–1.4822	40	39–44	7
8	Oleo oil	2 to 8	0.914–0.919	15	193–198	56–60				8
9	Lard oil	– 2 to 4	0.913–0.919	15.5	195–398	65–80	1.4702–1.4720	15.5	0.6	9
10	Neatsfoot oil	– 2 to 10	0.913–0.916	15.5	192–200	66–73	1.4695–1.4708	15		10
11	Seal oil	– 2 to –3	0.924–0.926	15	189–196	127–159	1.474	25	0.38–1.4	11
12	Bone fat	15 to 17	0.914–0.916	15	185–198	46–56			0.5 –1.8	12
13	Whale oil	– 2 to 0	0.920–0.925	15.5	188–194	110–128	1.4723–1.4749	25	0.92–3.7	13
14	Porpoise-jaw oil		0.9258	15	254–272	22–50			16–17	14
15	Dolphin oil	– 3 to 5	0.908–0.930	15	197–203	100–125	1.4708	15	2.0	15
16	Turtle oil				209–211		1.4677	30		16

CONSTANTS FOR FISH OILS AND FISH-LIVER OILS

		Solidifying Point °C.	Specific Gravity Value	Specific Gravity Temp. °C.	Saponification Value	Iodine Value	Refractive Index Value	Refractive Index Temp. °C.	Unsaponifiable Matter, %	
1	Menhaden oil	– 5	0.925–0.935	15.5	189–193	139–173	1.478	25	1.6–6.7	1
2	Sardine oil	20 to 22	0.927–0.933	15	189–196	181–193	1.4802–1.4808	20	0.5–1.4	2
3	Salmon oil		0.9258	15.5	182–188	161.4				3
4	Herring oil		0.920–0.939	15.5	171–194	123–142	1.4665–1.4729	25	0.99–10.7	4
5	Cod-liver oil	–10 to 0	0.920–0.925	15.5	182–189	135–168	1.4800–1.4852	15	0.5–9.9	5
6	Cod oil, Newfoundland		0.925–0.935	15.5	about 190	about 129				6
7	Halibut-liver oil									7
8	Shark-liver oil		0.916–0.919	15	161–164	114–144			5.5–10.2	8

CONSTANTS FOR VEGETABLE FATS AND OILS

		Solidifying Point °C.	Specific Gravity		Saponification Value	Iodine Value	Refractive Index		Unsaponifiable Matter, %	
			Value	Temp. °C.			Value	Temp. °C.		
1	Cocoa butter	21 to 23	0.950-0.976	15	192-202	32-41	1.456-1.458	40		1
2	Japan wax	40 to 46	0.970-0.999	15.5	210-237	5-12	1.448-1.449		1.1-1.6	2
3	Bayberry wax	25	0.933	15	198-199	68-80				3
4	Palm oil	35 to 42	0.920-0.945	15.5	196-205	51-57	1.4510	60		4
5	Chinese vegetable tallow	24 to 34	0.918-0.913	15	198-206	28-50	1.4510			5
6	Shea butter		0.917	15	179-192	54-63			5-9	6
7	Cottonseed oil	- 1 to 0	0.922-0.930	15	191-198	104-115	1.4737-1.4757	15.5	0.73-1.64	7
8	Cottonseed stearin	16 to 22	0.919-0.923	15	195	89-94	1.4700-1.4725	25		8
9	Tung oil	<17	0.936-0.943	15	190-197	150-165	1.5179	20	0.44	9
10	Oiticica oil		0.969	15	188-189	180				10
11	Peanut oil	- 3 to 3	0.911-0.922	15.5	186-197	85-103	1.4707-1.4731	15.5	0.54-0.94	11
12	Sesame oil	- 4 to -6	0.921-0.925	15.5	188-193	103-114	1.4748-1.4762	15.5	0.95-1.32	12
13	Soybean oil	-10 to -16	0.920-0.925	15.5	190-200	121-139	1.476 -1.4775	15.5		13
14	Palm-kernel oil	21 to 28	0.925-0.935	15.5	242-250	10-17	1.4431	60		14
15	Cocoanut oil	14 to 22	0.925-0.935	15	246-268	8-10	1.4481-1.4497	40	0.2	15
16	Babassu oil		0.869	100	246-250	12-16			0.5	16
17	Olive oil	- 6 to 2	0.916-0.920	15.5	185-296	77-91	1.4698-1.4716	15	0.46-1.0	17
18	Teaseed oil		0.920	15	190-194	91				18
19	Sunflower oil	-17 to -19	0.924-0.926	15	188-194	119-135	1.461	160	0.31	19
20	Poppyseed oil	-16 to -18	0.924-0.927	15.5	189-197	133-157.5	1.4766-1.4774	15.5	0.43	20
21	Linseed oil, raw	-17 to -27	0.931-0.938	15	190-195	171-201	1.4820-1.4852	15	0.4-1.0	21
22	Linseed oil, boiled		0.935-1.186		>186	>160			>2.5	22
23	Perilla oil		0.930-0.937	15	189.6	185-206	1.4825	15		23
24	Rapeseed oil	- 2 to -10	0.913-0.916	15.5	167-169	96-104	1.4720-1.4757	15	0.58-1.0	24
25	Corn oil	-10 to -20	0.920-0.926	15.5	188-193	113-129	1.4760-1.4768	15.5	1.35-2.86	25
26	Hempseed oil	-15 to -28	0.925-0.928	15	192-195	148-160			1.08	26
27	Croton oil	- 8 to -18	0.937-0.943	15	210-215	102-107	1.4757-1.4768	27	0.55	27
28	Walnut oil	-15 to -27	0.925-0.926	15	188-197	142-152	1.469 -1.471	40		28
29	Sweet almond oil	-15 to - 20	0.916-0.920	15.5	189-195	93-104	1.4685-1.4693	25		29
30	Peach-kernel oil	<-20	0.918-0.922	15	189-193	93-109	1.4697-1.4705	25		30
31	Apricot-kernel oil	-17	0.915-0.926	15	191-198	100-109	1.4636-1.4705	25		31
32	Castor oil	-10 to -18	0.950-0.968	15.5	177-186	83-88.5	1.4799-1.4803	15		32
33	Chaulmoogra oil	20 to 25	0.943-0.954	15	196-213	97.6-110.4	1.4777-1.4779	25	2.4-2.6	33
34	Wheat-germ oil		0.9268	25	186.5	125.6	1.4762	20	4.7	34

CHAPTER XXVI

WAXES

The true **waxes** are a class of esters. They differ from the fats and oils in being esters of high molecular-weight fatty acids with high molecular-weight monohydric alcohols, rather than of the trihydric alcohol, glycerine. Examples of true waxes are spermaceti, which consists mainly of cetyl palmitate, and beeswax, which is mostly myricyl palmitate. They are natural products and therefore often contain free alcohols, free fatty acids, hydrocarbons and other impurities, in addition to dirt and other foreign matter. Physically they are usually harder than the fats, more brittle and less greasy. They may be of vegetable or animal origin, such as carnauba wax and beeswax, respectively.

A classification by physical properties is sometimes, but not generally, used. By it all materials with wax-like characteristics are grouped together. This produces a heterogeneous class with fats such as bayberry wax and Japan wax, and hydrocarbons such as ozokerite, ceresin, montan wax and paraffin included. There is no simple form of classification. The usual terminology leads to confusion in calling products waxes which are not so in fact, and conversely in calling some true waxes by other names. The commercial waxes are relatively limited in number.

Waxes may be sold in the crude state in which they are found in nature, or they may be separated from solid and water-soluble impurities by melting up with boiling water and filtering. Crude wax is darker in color than the refined. Some waxes are bleached with oxidizing agents. The waxes are more individual in their solubility than the oils and fats. They are miscible in all proportions with oils and fats. The melting point of a wax is often taken as a general indication of its character, as hardness is a direct function of melting point.

For convenience the properties have been grouped in a table at the end of this chapter.

Carnauba wax occurs on the leaves of a species of palm which grows in Brazil. It is soluble in boiling alcohol, hot turpentine, or carbon tetrachloride. The crude wax is scraped from the dried leaves, melted in hot water and drawn off from the surface of the water. The crude product is greenish brown, but refinement with sulfuric acid gives a yellow wax. It is sometimes admixed with paraffin, which modifies its properties. Carnauba wax contains the ester of myricyl alcohol and cerotic acid, as well as the free alcohol and free acid. Grades sold are numbers 1, 2 and 3 of yellow or refined, north country, and chalky. Of these the number 1 grade is best. North country is a crude grade. Chalky has the physical appearance implied by the name and contains some dirt. It is said to be the crude, melted in hot water to separate stones and some dirt. Practically speaking, the important grades are No. 1 yellow, No. 2 yellow, No. 2 north country, No. 3 chalky and No. 3 north country. Carnauba wax is used in floor wax, in polishes for shoes, furniture and automobiles, insulating compositions, leather finishes and phonograph records, as well as for miscellaneous purposes. It is the hardest and most expensive of the common waxes.

Chinese wax, vegetable spermaceti, insect wax or **Chinese tree wax** is a yellow to white, crystalline solid somewhat resembling spermaceti but being harder and more friable. It has very little odor. It is soluble in benzene and slightly soluble in alcohol or ether. The wax is secreted by a scale insect common to China and India and is deposited on certain species of ash trees. The material is collected, melted and filtered to remove dirt. The wax consists essentially of ceryl cerotate and is used in making candles, as a paper size, and in various types of polishes. The supply is limited and erratic.

Candelilla wax occurs as a coating on the Mexican shrub, candelilla, from which it is obtained by melting the wax with hot water and skimming it off as it rises to the surface of the liquid. Candelilla wax is soluble in turpentine, hot chloroform and carbon tetrachloride. It is classed as a hard wax. The brown wax is refined to give a yellow product by treatment with sulfuric acid. It is used for the same purposes as carnauba wax and in general is somewhat less satisfactory and less expensive.

Beeswax is secreted by the bee and used for the construction of honeycomb. It is soluble in ether, chloroform, benzene, carbon bisulfide, slightly soluble in cold alcohol but more soluble in boiling alcohol. It is melted with hot water, then strained and the residue pressed to give more wax. Beeswax contains myricyl palmitate, cerotic acid and some hydrocarbons. The natural wax is yellow in color and may be bleached by the action of sunlight or by treatment with oxidizing agents. Grades sold are pure bleached white beeswax in slabs, crude yellow wax from Africa, Brazil and Chile, and refined yellow wax in slabs. The bleached wax is used in ointments, cosmetic creams, candle making, molded wax products, etc. The yellow wax is used in floor waxes, shoe polish, sizing compounds, lithographing, leather dressing and candles.

Spermaceti is a crystalline wax obtained from sperm oil, found in the head of the sperm whale. It is soluble in chloroform, ether, carbon bisulfide or boiling alcohol, and slightly soluble in petroleum ether. It is filtered under pressure to separate stearin, and washed with hot water containing a little alkali, followed by plain water. The wax consists mainly of cetyl palmitate. It is pearly white and is sold in blocks and cakes for use in ointments, candles, etc.

Sperm oil or **sperm whale oil** is a light yellow liquid obtained from the head and blubber cavities of the sperm whale. It is a true wax, although a liquid, and is soluble in chloroform, ether and benzene. Grades are bleached and natural, 38° F. and 45° F. cold test, or occasionally refined and crude. It is used as a high-grade lubricating oil for light machinery such as clocks, watches and scientific instruments, and is extremely expensive.

Ambergris is a waxy material which may be gray, yellow, white or black in color. It is a morbid concretion of the sperm whale, in whose alimentary canal it may occur. The material is also found as a floating mass in tropical oceans, but so rarely that it is of great value. It is soluble in ether, chloroform and fats. Ambergris melts at about 60°C. and contains 80-90 per cent of cholesterin along with fatty oils. It is medically an antispasmodic, aphrodisiac, stimulant and antihysteric. Its major use is in perfumes as a fixative.

PHYSICAL CONSTANTS OF WAXES

Wax	Solidifying Point ° C.	Specific gravity at 15° C.	Saponification value	Refractive Index
Carnauba	80-87	0.990- 0.999	79-95	1.452-1.454 at 84°
Chinese wax	m.p. 80-33	about 0.970	80-93	
Candelilla	m.p. 67-70	0.950- 0.990	about 65	about 1.455 at M.P.
Beeswax	61-63	0.958- 0.970	90-102	1.430-1.445 at 75°
Spermaceti	42-47	0.942- 0.960	123-135	
Sperm oil	about 15	0.878- 0.883	123-147	1.466-1.467 at 15.5°

CHAPTER XXVII

ETHERS

Ethers are organic compounds in which two organic groups are joined together through an oxygen atom. The groups may be simple alkyl radicals as in diethyl ether, aryl radicals as in diphenyl ether, or one or both may be complex. Chemically the ethers have the structure of an oxide. They have nothing in common with inorganic oxides, which frequently react with water to form acids or bases. Ethers are very stable. They are useful because of their solvent properties for other organic materials but being unreactive, they are not commonly useful other than as solvents, in organic synthesis. Therefore the group of commercial products is limited. Some products are called ethers which do not have that structure and are not in this chapter, such as acetic ether which is ethyl acetate, a true ester.

Ethyl ether, sulfuric ether, diethyl ether or **diethyl oxide,** $(C_2H_5)_2O$, is a colorless liquid moderately soluble in water and miscible with alcohol. It is the most widely used member of the class and is commonly called **ether.** This ether is made by distilling alcohol with concentrated sulfuric acid. Alcohol has to be supplied continuously as the ether distils over. The distillate is purified by redistilling from lime and calcium chloride. The colorless liquid is highly volatile and inflammable. Alcohol and water are commonly present unless otherwise specified, U.S.P. ether containing 96-98 per cent of ether. Peroxides, which develop on exposure to air, must be absent in ether for anesthesia, which therefore commands a substantial premium. The peroxides are dangerously explosive in distillation and should be absent by test with aqueous solutions of inorganic iodides. They do not form to a serious degree in the presence of much water and can be destroyed by addition of reducing agents such as sulfites. An 1880 U.S.P. grade is also quoted at a premium. Washed ether is free from alcohol but not from water. Concentrated ether is the anhydrous grade free from alcohol and water but not free from peroxides. While all ether is synthetic, the commercial grade is quoted as synthetic ether. Aside from serving as an anesthetic it is used as a solvent in the manufacture of smokeless powder, for extraction of fats, oils, resins, gums and alkaloids, in the manufacture of rayon and pyroxylin, and as a solvent in many organic reactions.

Ethylene oxide, $\underline{CH_2OCH_2}$, is a colorless, inflammable gas at ordinary temperatures since it boils at 13.5° C. It has a pleasant odor and is miscible with water and soluble in most organic solvents. Manufacture is by the action of sodium hydroxide on ethylene chlorohydrin. Ethylene oxide is sold in pressure cylinders for use in organic synthesis and in fumigation. It is highly toxic to larvae but only slightly so to humans, and therefore is used for destroying infestation of packaged foodstuffs, grain, etc. A mixture of 90 per cent of carbon dioxide and 10 per cent of ethylene oxide is sold for the purpose, is noninflammable, and the carbon dioxide increases the effectiveness of the ethylene oxide. **Propylene oxide,** $CH_3\underline{CHCH_2O}$, is similar but liquid at room temperature and somewhat less toxic to insects.

Diethylene oxide or **dioxan** is the 1,4 compound, $(CH_2OCH_2)_2$, prepared by powerful dehydration of ethylene glycol. The colorless liquid has a faint, pleasant odor and is similar in many properties to alcohol. It is miscible with water and most solvents. A constant-boiling mixture is formed with 20 per cent of water. Uses are mainly as a solvent.

Dichloroethyl ether, $(CH_2ClCH_2)_2O$, is a colorless, inflammable liquid of low volatility prepared by the chlorination of ethyl ether. It is very soluble in alcohol or ether and is used as a solvent, such as in paint and varnish removers, spotting compounds, wetting-out agents, for the improvement of the quality of lubricating oils by extraction, etc.

Isopropyl ether, $[(CH_3)_2CH]_2O$, is a colorless, inflammable solvent, slightly soluble in water and miscible with alcohol or ether. It is prepared from isopropyl alcohol by a method analogous to that for ethyl ether, and is used as a solvent for vegetable, animal and mineral oils, resins and waxes. This ether is mixed with alcohols for special solvent purposes. It forms peroxides even more readily than ethyl ether.

Butyric ether or butyl ether, $(C_4H_9)_2O$, is a colorless liquid miscible with the majority of organic solvents. It is produced from butyl alcohol by methods similar to those used for ethyl ether and is used as a high-boiling solvent for gums, resins, oils, etc.

Amyl ether, diamyl ether or amyl oxide, $(C_5H_{11})_2O$, is a colorless to light yellow liquid miscible with alcohol or ether. It is a mixture of normal and isoamyl ethers, is prepared by heating amyl alcohol with amyl chloride, and is used as a solvent.

Ethylene glycol monomethyl ether, $CH_2OHCH_2OCH_3$, **ethylene glycol monoethyl ether,** $CH_2OHCH_2OC_2H_5$, **ethylene glycol monobutyl ether,** $CH_2OHCH_2OC_4H_9$, **diethylene glycol monomethyl ether** or **methyl Carbitol,** $CH_2OHCH_2OCH_2CH_2OCH_3$, **diethylene glycol monoethyl ether** or **Carbitol,** $CH_2OHCH_2OCH_2CH_2OC_2H_5$, and **diethylene glycol monobutyl ether** or **butyl Carbitol,** $CH_2OHCH_2OCH_2CH_2OC_4H_9$, are a series of solvents prepared synthetically. Carbitol is a registered trade name. They are colorless and very soluble in alcohol or ether, and are both ethers and alcohols in each case. They are used to dissolve organic compounds such as dyes, nitrocellulose, and cellulose acetate, and in printing textiles. Their uses are those requiring ethers of varying and relatively low volatility. Special uses are as adhesives for sealing coated cellophane, in cosmetics, in paint and varnish removers, in wetting agents, etc.

Phenyl ether, diphenyl ether or **diphenyl oxide,** $(C_6H_5)_2O$, is a white solid melting just above room temperature, and is soluble in alcohol or ether. It is formed by heating phenol with anhydrous zinc chloride or by the interaction of chlorobenzene and sodium phenate heated under pressure. The commercial supply is a by-product from the process of manufacture of phenol from chlorobenzene. It has an odor like that of geranium and is used in inexpensive perfume, for some synthetic purposes, and as an ingredient of heat-transfer compositions. The latter use is strictly limited by its high price.

Acetophenetidine, phenacetin, ***para*-acetaminophenetol** or ***p*-acetaminophenetol,** $C_6H_5OC_6H_4NHOCCH_3$, is prepared as a white crystalline product from *para*-phenetidine by treatment with glacial acetic acid, or by the reaction of ethyl bromide and *para*-acetaminophenol. It is a U.S.P. product melting at 134-5° C., moderately soluble in alcohol and slightly soluble in ether, and is used in medicine as an antipyretic.

Methyl-*para*-cresol or **methyl-*p*-cresol,** $CH_3C_6H_4OCH_3$, is a colorless liquid miscible with ethers and used with narcissus, lilac, hyacinth and similar odors.

Anethol, ***para*-allylphenylmethyl ether** or ***p*-allylphenylmethyl ether,** $C_3H_5C_6H_4OCH_3$, is obtained from anise and fennel oils and is purified by fractional distillation. The colorless crystals melt at about 21° C., so that the product is liquid at ordinary temperatures. It is soluble in alcohol and miscible with ether. Anethol has an odor of anise, and aside from use in organic synthesis, is a flavoring material, as in dentifrices, an odorant for soaps, and a reagent in color photography. **Isoamylbenzyl ether,** $C_5H_{11}OCH_2C_6H_5$, is closely related and has a gardenia odor.

Safrol, $C_3H_5C_6H_3O_2CH_2$, is the methylene ether of allyl catechol, 1-allyl-3,4-methylene dioxybenzene. It has a sassafras odor and is obtained from oil of sassafras, of which it constitutes about 80 per cent. Safrol is also present in a lesser amount in several other essential oils, such as camphor oil. The colorless to light yellow oily liquid is very soluble in alcohol or ether, and is sometimes called **oil of safrol.** The uses are as an odorant in low-price perfumes or soaps, for denaturing soap fats, in organic synthesis, such as of piperonal, and in medicine, largely to replace oil of sassafras.

Yara yara, ***beta*-naphthylmethyl ether** or **β-naphthylmethyl ether,** $C_{10}H_7OCH_3$, is prepared by heating *beta*-naphthol and methyl alcohol together in the presence of a dehydrating agent such as sulfuric acid. The white crystalline product has an orange blossom odor, and is slightly soluble in water or alcohol and very soluble in ether. It is used in inexpensive orange or jasmine perfumes and in soaps, both as a odorant and as a fixative. It is stable to both acids and alkalies. **Nerolin,** ***beta*-naphthylethyl ether** or **β-naphthylethyl ether,** $C_{10}H_7OC_2H_5$, is similar to the methyl ether, yara yara, in preparation, in properties and uses.

Ethyl isoeugenol, $C_3H_5(CH_3O)C_6H_3OC_2H_5$, **methyl eugenol,** $C_3H_5(CH_3O)C_6H_3OCH_3$, and the isomeric **methyl isoeugenol** are synthetic white, crystalline powders, prepared by dehydration methods, soluble in alcohol or ether, and used as sweetening agents and fixatives in odorants. **Benzyl isoeugenol,** $C_3H_5(CH_3O)C_6H_3OCH_2C_6H_5$, is a similar synthetic ether sold as a white powder of low density, soluble in alcohol or ether. It is a fixative and odorant for perfumes such as carnation, violet, rose, etc.

Dimethyl hydroquinone, $C_6H_4(OCH_3)_2$, is the ether resulting from reaction of hydroquinone with methyl iodide in the presence of caustic potash. It is a colorless, crystalline compound soluble in alcohol or ether and used as a fixative in odorants.

Paraldehyde, $(C_2H_4O)_3$, is a true cyclic ether but from its derivation by polymerization of acetaldehyde has been discussed with that compound.

Ethyl cellulose or **cellulose ether** is the ether formed by reaction of ethyl alcohol with cellulose in the presence of dehydrating agents. Different compositions vary in solubility, some being alcohol-soluble, some soluble in cold water but not in hot, others soluble in either hot or cold water. Films of ethyl cellulose are noted for their flexibility at low temperatures. Uses are in fabric finishing such as for "crease proofing," as a semiplasticizer in plastics and protective coatings, etc. The ether would compete with cellulose esters such as the nitrate and acetate in many applications if the price were lower, as seems definitely possible over a period of years.

Salicin, $(HO)_4C_6H_7O_2C_6H_4CH_2OH$, is a white crystalline glucoside found in the bark and leaves of several species of poplar and willow trees. It is an ether of salicyl alcohol and glucose. Salicin is moderately soluble in cold water or alcohol.

It is used in medicine as a tonic, antipyretic and antirheumatic, having the general properties of salicylic acid.

Saponin is a mixture of glucosides which may be represented in general by the formula, $C_nH_{2n-8}O_{10}$. Saponin occurs in plants such as soapbark, soapwort, senega, etc., and may be obtained by extraction. The white to yellow or brown amorphous product has an unpleasant odor and is easily soluble in water or hot alcohol. Some types are toxic, others not. Both crude and purified grades are available. Saponin is used as a foam producer, in fire extinguishers, beverages, textile sizes, etc. It is also used as an expensive form of detergent. In beverages only 1 part in 100,000 is required to give a foam.

CHAPTER XXVIII

ORGANIC DYES

With rare exceptions, the dyes in modern use are synthetic in origin. They are usually referred to as coal-tar dyes because they are built up from such simple hydrocarbons as benzene, methyl derivatives of benzene, naphthalene and anthracene, all of which can be obtained directly from coal tar by fractional distillation and subsequent purification. These relatively simple hydrocarbons are converted into intermediate products such as aniline, naphthols, benzaldehyde, benzidine, anthraquinone, phthallic anhydride, nitroanilines, etc. These in turn are changed into the more complex dyestuffs by chemical addition of other groups, or by combining some of the intermediate compounds themselves. It may be seen that an almost limitless number of compounds can be synthesized in this fashion.

Chemical classification of dyes is by the chromophore or color-producing group present in the compound. The azo dyes contain the grouping R-N:N-R, other types other characteristic groups.

Acid dyes are usually sodium salts of a color agent which is structurally an acid. They are usually applied in an acid medium. Acid dyes are the most important group used for wool dyeing, and are applied to hosiery, carpet yarns, suitings, dress goods and hat materials, and to silk to a lesser extent. They have little affinity for vegetable fibers except jute, and in general they are used on goods not requiring repeated washing. Members of this class are superior to direct and mordant dyes but inferior to basic dyes in purity of shade. Acid dyes are available in a wide color range and are usually fairly fast to light and acids but have a tendency to bleed on washing. They bleed less from wool than from silk. Many are among the lowest-price dyes, simply and inexpensively applied. The class shades into mordant dyes, as some are "afterchromed" to produce fastness. Generally speaking, they are nitro or azo compounds, or sulfonated basic dyes of the triphenylmethane type.

Basic dyes are historically the oldest class, including mauvine or Perkin violet, discovered in 1856, the first synthetic dyestuff produced commercially. They are the best dyes for brilliancy of shade and purity of tone. While they have high tinctorial power they are not very fast to light or washing. Basic dyes are used for dyeing and printing cotton, giving bright colors of low fastness. Other uses are in dyeing paper and jute, and in lithographic inks, typewriter ribbons, copy paper, pencils, etc. A few are used on wool. When applied on vegetable fibers they are mordanted with tannic acid. Their importance has lessened with the increased use of direct and sulfur dyes, which are often more fast and more economical. They may be triphenylmethane derivatives, azines, azos, thioazines, thioazols or acridines.

Direct cotton dyes or **substantive dyes** attach themselves to vegetable fibers in a neutral or alkaline bath to give full shades without the use of mordants. They are also used on cotton-wool or cotton-silk mixtures and linen, silk, paper and wool, particularly low-grade wool. Direct dyes vary widely in fastness and have a tendency to run in washing. Many are sensitive to acids and sunlight; others are fast to these agents. Some are coupled with intermediates or aftertreated with metallic salts or formaldehyde. They are largely either thiazoles or azo compounds derived from benzidine, toluidine, diamino stilbene or similar groupings.

Mordant dyes are used with mordants such as aluminum, chromium, iron or tin. They are often called **chrome dyes,** which are, strictly speaking, one class of mordant dyes. On wool they give fastness to light, washing, etc. They are important in cotton printing. Since many are derived from alizarin they have been called **alizarin dyes.** Some alizarin dyes are acid dyes and can be used without mordant. The application of the mordant may precede, accompany or follow application of the dyestuff. The labor cost is high in their application. They are largely of the anthracene, azo, oxazine, triphenylmethane, nitroso, oxyquinone or xanthone types. The most important is alizarin, a Turkey red for cotton, formerly produced from madder root but for many decades now from anthracene.

Sulfur dyes largely produce heavy deep shades such as blue, green, brown and black. They are used mainly on cotton or cotton warps to be woven with wool. Sulfur dyes are also applied to linen and artificial silk. They are very fast to washing and to acids and alkalies, which recommends them for cross-dyeing. These dyes are usually fast to light but rarely to chlorine in laundering. They are applied in sodium sulfide solution and often after-treated to improve their fastness. As produced by fusion of intermediates with sulfur they are not distinct compounds and have relatively low color value.

Vat dyes are important on cottons because laundry fast. They are applied as solid colors or prints, their use for solid colors being limited by their high price. They are very fast to light, washing, acids, alkalies and usually to chlorine. No other class is as fast to chlorine. The usual types are derivatives of indigo, anthraquinone or carbazole.

Natural dyestuffs are a fast declining class. They may require special methods of application. Some, such as indigo or alizarin, have been replaced by synthetic duplicates, others, such as bixin and curcumin, by other dyes of similar color.

Color lake dyes are used in preparation of the class of pigments known as **color lakes.** These consist of the color agent and a carrier. Requirements are high tinctorial power, brightness and fastness to light, alkali, acids and exposure. The carriers are usually aluminum hydroxide, zinc oxide, lithopone, barytes, whiting, china clay or ocher. Precipitating agents are barium chloride, lead salts, aluminum hydroxide, tannin and tartar emetic. The dyes used include acid, basic and mordant types. Some azo dyes are produced on the carrier, others are precipitated as an insoluble salt of a metal. Such lakes are ground and used in paints, inks, artists' colors, wallpaper, rubber, etc. The dyestuff itself sold for use as a pigment, is known as an organic **toner.**

Acetate rayon takes very few of the above dyes, so that special **acetate-rayon dyes** were developed for the purpose. To these belong the ionamines, in which insoluble compounds have been made soluble by the introduction of a methylated sulfonic group which splits off during the dyeing. In other cases insoluble dyes have been prepared and used in colloidal suspension with the aid of sulfonated castor oil. These dyes are are not taken up by cotton, linen or viscose rayon. The latter can be dyed with direct cotton dyes.

Certified food colors are dyes of a quality established experimentally as nontoxic in substantially larger quantities than would ever be used commercially. They are fundamentally the same classes of dyes as previously discussed, specially purified to insure relative freedom from arsenic, lead and other heavy metals, and checked as to analysis by the Department of Agriculture. Each can of dye bears a lot number assigned when the official analysis is made. Those listed in the table are the straight colors. Blends are often sold under trade names, thus saving the manufacturers from the necessary labor of accurate weighing and mixing to get a reliable, duplicable tone or shade.

The relative amounts of dyes used in commercial processes will vary radicallv. For dyeing of fabric, the amount required may vary from a fraction of a per cent for a light shade to as much as 10 per cent for a dark shade. In other applications the quantity needed will depend very largely on the transparency of the medium. A very small amount will lend substantial color to a transparent material, a large amount will be required for a highly opaque material.

A systematic and purely arbitrary classification of dyes by chemical constitution was first developed by Schultz and Julius in 1888 and revised from time to time by Schultz. The present system used here is that of the "Colour Index" of F. W. Rowe, as published by the Society of Dyers and Colourists, of Bradford, England. This is based on the German system, revised and enlarged to a set of 26 groups as follows:

	Chemical Class	Color Index No.
1.	Nitroso	1-6
2.	Nitro	7-14
3.	Mono-azo	15-229
4.	Dis-azo	230-530
5.	Tris-azo	531-605
6.	Tetrazo	606-619
7.	Stilbene	620-635
8.	Pyrazolone	636-654
9.	Ketonimine	655-656
10.	Triphenylmethane and Diphenylmethane	657-738
11.	Xanthene	739-784
12.	Acridine	785-799
13.	Quinoline	800-811
14.	Thiazole	812-817
15.	Indamine	818-820
16.	Indophenol	821-823
17.	Azine	824-869
18.	Aniline black and allied dyes	870-875
19.	Oxazine	876-919
20.	Thiazine	920-932
21.	Sulfide	933-1012
22.	Hydroxyketone, hydroxyquinone and hydroxylactone	1013-1026
23.	Anthraquinone (acid and mordant)	1027-1093
24.	Anthraquinone (vat)	1094-1175
25.	Arylido quinone (vat)	1176
26.	Indigoid	1177-1230

While these data are sufficient for identification of the type of structure of any dyestuff in the tabulation, the type has been given as a matter of convenience.

Synthetic dyestuffs are sold by trade names, which may or may not indicate the color. Sometimes the name is followed by one or more letters. These may indicate the color, as R for red, B for blue, G for yellow from the German word gelb;

and also the intensity of color, 2R being a deeper red than R; or the letters may be used as a manufacturer's designation and be without general significance.

In the table which follows are given data on somewhat over 125 such dyes, numerically about 10 per cent of those in the color index. These are dyes in sufficiently general use to be quoted. Any one dye may have more than a dozen names so that this list is more comprehensive than may appear from the number of dyestuffs listed. It includes the major tonnage of dyestuffs. The color-index number is usually sufficient for identification, but in some cases more than one name in general use has been included for simplicity in identification. In such cases the first name is that more positive in identification, and the one in parentheses a more general trade name.

Following the table are a few natural dyestuffs, or special synthetic dyes of such importance as to indicate the desirability of individual treatment.

COMMON DYESTUFFS READILY AVAILABLE

Color Index	General Name	Chemical Structure	Type and Comment
5	Naphthol green B	Nitroso	Acid
10	Naphthol yellow S	Nitro	Acid
15	Amidoazobenzene yellow	Mono-azo	Oil
17	Amidoazotoluene yellow	Mono-azo	Oil- and spirit-soluble
20	Chrysoidin G base	Mono-azo	Spirit-soluble
20	Chrysoidin G	Mono-azo	Basic Orange
21	Chrysoidin R base	Mono-azo	Spirit-soluble
21	Chrysoidin R	Mono-azo	Basic Orange
22	Yellow AB	Mono-azo	Oil Certified food color
24	Sudan 1	Mono-azo	Oil Orange
27	Orange G	Mono-azo	Acid
31	Amidonaphthol red G	Mono-azo	Acid
36	Alizarin yellow 2 G (Chrome yellow 2 G)	Mono-azo	Acid and Mordant
40	Alizarin yellow R (Chrome yellow R)	Mono-azo	Acid and Mordant
53	Victoria violet	Mono-azo	Acid
57	Amidonaphthol red 6B	Mono-azo	Acid
61	Oil yellow OB (yellow OB)	Mono-azo	Oil Certified food color
73	Sudan II	Mono-azo	Oil Scarlet
79	Ponceau R	Mono-azo	Acid Scarlet
80	Ponceau 3R	Mono-azo	Acid Certified food color

COMMON DYESTUFFS READILY AVAILABLE—*Continued*

Color Index	General Name	Chemical Structure	Type and Comment
88	Fast red B	Mono-azo	Acid
138	Metanil yellow	Mono-azo	Acid
150	Orange I	Mono-azo	Acid Certified food color
151	Orange II (Orange Y)	Mono-azo	Acid
161	Orange R	Mono-azo	Acid
165	Lake red C	Mono-azo	Lake
176	Fast red A	Mono-azo	Acid
179	Azorubin	Mono-azo	Acid and mordant Blue
180	Diamond blue 3 B (Fast red VR)	Mono-azo	Acid and mordant Blue with red cast
183	Crocein scarlet 3BX	Mono-azo	Acid
184	Amaranth	Mono-azo	Acid Red Certified food colo
185	Cochineal red A	Mono-azo	Acid
189	Lithol red R, paste or powder (Lake red R)	Mono-azo	Lake
202	Erichrome blue black U (Chrome blue black U)	Mono-azo	Acid and mordant
204	Erichrome black A (Chrome black A)	Mono-azo	Acid and mordant
208	Sulphur acid blue R (Fast red blue R)	Mono-azo	Acid
216	Acid alizarin red B (Chrome red B)	Mono-azo	Acid and mordant
234	Resorcin brown Y	Dis-azo	Acid
235	Resorcin dark brown R	Dis-azo	Acid
246	Naphthol blue black S	Dis-azo	Acid
252	Brilliant crocein M	Dis-azo	Acid Scarlet
258	Sudan IV	Dis-azo	Oil Scarlet
262	Cloth red 2B	Dis-azo	Acid and mordant
289	Sulphon cyanin 5R Ex (Fast cyanin 5R)	Dis-azo	Acid Navy blue
299	Diamond black F (Chrome black F)	Dis-azo	Acid and mordant
307	Sulphon cyanin black B (Fast cyanin black B)	Dis-azo	Acid
326	Benzo fast scarlet (Direct fast scarlet)	Dis-azo	Direct
331	Bismarck brown G	Dis-azo	Basic
332	Bismarck brown R	Dis-azo	Basic and spirit-soluble
364	Brilliant yellow (Paper yellow)	Dis-azo	Direct General
365	Chrysophenin G	Dis-azo	Direct Yellow
382	Diamine scarlet B (Direct scarlet B)	Dis-azo	Direct
387	Trisulfon violet B (Direct violet B)	Dis-azo	Direct

Common Dyestuffs Readily Available—*Continued*

Color Index	General Name	Chemical Structure	Type and Comment
394	Diamine violet N (Direct violet N)	Dis-azo	Direct
401	Diamine black BH (Developed black BHN)	Dis-azo	Direct and developed
406	Benzo blue BB (Direct blue 2B)	Dis-azo	Direct
415	Benzo orange R (Direct orange R)	Dis-azo	Direct
419	Diamin fast red F (Direct fast red F)	Dis-azo	Direct
420	Diamin brown M	Dis-azo	Direct
448	Benzopurpurin 4B	Dis-azo	Direct Red
495	Benzopurpurin 10B	Dis-azo	Direct Red
502	Benzo azurin G (Direct azurin G)	Dis-azo	Direct Blue
512	Benzo blue RW (Direct blue RW)	Dis-azo	Direct
518	Diamin sky blue FF (Direct pure blue 6B)	Dis-azo	Direct
520	Benzo sky blue (Direct pure blue)	Dis-azo	Direct
539	Columbia black FF ex (Direct flat black FF)	Tris-azo	Direct
581	Direct deep black EW ex (Direct black EW)	Tris-azo	Direct
582	Direct deep black RW ex (Direct black RX)	Tris-azo	Direct
593	Diamine green B (Direct green B)	Tris-azo	Direct
594	Diamine green G (Direct green G)	Tris-azo	Direct
596	Benzamine brown 3GO (Direct brown 3GO)	Tris-azo	Direct
620	Sun yellow (Direct yellow R)	Stilbene	Direct
636	Fast light yellow	Pyrazolone	Acid
639	Xylene light yellow	Pyrazolone	Acid
640	Tartrazine	Pyrazolone	Acid Yellow Certified food color
655	Auramine base	Ketonimine	Spirit-soluble Yellow
655	Auramine	Ketonimine	Basic or mordant Yellow
657	Malachite green base	Triphenylmethane	Spirit-soluble
657	Malachite green	Triphenylmethane	Basic
662	Brilliant green	Triphenylmethane	Basic
666	Guinea green B	Triphenylmethane	Acid Certified food color

COMMON DYESTUFFS READILY AVAILABLE—*Continued*

Color Index	General Name	Chemical Structure	Type and Comment
670	Light green, SF yellowish	Triphenylmethane	Acid Certified food color
671	Brilliant blue	Triphenylmethane	Basic Certified food color
677	Fuchsine base (Magenta base)	Triphenylmethane	Spirit-soluble Red
677	Fuchsine	Triphenylmethane	Basic Red
680	Methyl violet base	Triphenylmethane	Spirit-soluble
680	Methyl violet B	Triphenylmethane	Basic
680	Oil violet	Triphenylmethane	Oil
681	Crystal violet base	Triphenylmethane	Spirit-soluble
681	Crystal violet	Triphenylmethane	Basic
695	Acid violet 4BN	Triphenylmethane	Acid
698	Formyl violet S4B (Acid violet)	Triphenylmethane	Acid
714	Patent blue A	Triphenylmethane	Acid
729	Victoria blue B base	Triphenylmethane	Spirit-soluble
729	Victoria blue B	Triphenylmethane	Acid
737	Wool green S	Triphenylmethane	Acid
749	Rhodamine B	Xanthine	Acid Red
752	Rhodamine 6G	Xanthine	Acid Red
768	Eosine G	Xanthine	Acid Red
773	Erythrosine	Xanthine	Acid Red Certified food color
793	Phosphine	Acridine	Basic Yellow
800	Quinoline yellow spirit-soluble (Chinoline yellow SS)	Quinoline	Spirit-soluble
812	Primuline	Thiazole	Direct and developed Yellow
814	Chloramine yellow (Direct fast yellow)	Thiazole	Direct
841	Safranine	Azine	Basic Red
860	Induline, spirit-soluble	Azine	Spirit-soluble Blue-violet
861	Induline	Azine	Acid Blue-violet
864	Nigrosine, spirit-soluble	Azine	Spirit-soluble Black
865	Nigrosine	Azine	Acid Black
865	Nigrosine derivatives	Azine	Oil-soluble Black
873	Methylene gray	Aniline black	Basic

COMMON DYESTUFFS READILY AVAILABLE—*Continued*

Color Index	General Name	Chemical Structure	Type and Comment
909	New blue R	Oxazine	Basic
922	Methylene blue	Thiazine	Basic
	For U.S.P. grade see page 338.		
924	Methylene green B	Thiazine	Acid
1054	Alizarin saphirol B	Anthraquinone	Acid Blue
1075	Alizarin astrol B (Alizarin astrol base)	Anthraquinone	Spirit-soluble Blue
1078	Alizarin cyanin green base	Anthraquinone	Oil-soluble
1078	Alizarin cyanin green base	Anthraquinone	Acid and mordant
1080	Anthraquinone violet base	Anthraquinone	Oil-soluble
1177	Indigo	Indigoid	Vat Blue
	For natural indigo see page 338.		
1180	Indigotin IA or sodium indigo	Indigoid	Acid Blue Certified food color
	Benzo fast black L		Direct
	Zambesi black		Direct and developed
	Oil-soluble orange, red shade		Oil
	Oil-soluble brown		Oil
	Oil-soluble green		Oil
	Sulfur tan	Sulfur	Direct
	Sulfur brown	Sulfur	Direct
	Sulfur yellow	Sulfur	Direct
	Sulfur black	Sulfur	Direct
	Sulfur blue	Sulfur	Direct
	Sulfur maroon	Sulfur	Direct
	Sulfur olive	Sulfur	Direct
	Fast green FCF		Certified food color
	Sunset yellow FCF		Certified food color

Cochineal consists of the dried bodies of female cochineal insects of *Coccus cacti,* which thrive on various species of cactus grown in tropical countries for this purpose. According to U.S.P. standards the bodies of the insects enclose the young larvae. This dry powdered material serves as a red dye and contains about 10 per cent of a complex organic acid, carminic acid, as the active principle. When the insects are killed with dry heat, a gray powder is retained on the bodies. Grades sold are gray and Tenereffe silver. U.S.P. grades are whole and ground. The color is soluble in water or alcohol. The dye is used for coloring foods, toilet preparations, ink, textiles and for the manufacture of lakes. It is rarely used medicinally

Annatto is a salmon-colored dye obtained from the pulp of the seeds of *Bixa orellana,* a tree grown in the West Indies and

South America. This natural vegetable dye contains the coloring principles **bixin** and **orellin.** It is soluble in alcohol, ether and oils. Annatto paste is used mostly as a food dye, as for coloring butter, cheese and oils. It can also be used for dyeing silk and in wood stains. The seeds are also available.

Indigo is a blue dye obtained from the glucoside indican which occurs naturally in plants of the genus *Indigofera.* The natural product contains, in addition to 20-90 per cent of indigo blue, considerable amounts of indigo brown, indigo red and other coloring principles. Synthetic indigo consists of indigo blue or indigotin in practically pure form. Indigo is the most important vat dye. The fabric to be dyed with it is immersed in the colorless, reduced or leuco form of the dye in alkaline solution and then exposed to air, when the insoluble blue dye is formed by atmospheric oxidation. **Natural Madras indigo** is sold as an expensive product, not competitive in price with the synthetic grade. The synthetic product is quoted as a powder and liquid. It is used for printing and dyeing textiles, in ink, and for the production of indigo derivatives.

Methylene blue or **methylthionine chloride** is an important blue dye of the thiazine class. The U.S.P. grade is $C_{16}H_{18}N_3SCl,3H_2O$, and must contain 98.5 per cent of the anhydrous dyestuff when dried to constant weight. The technical product, not to be confused with the U.S.P. color, is $(C_{16}H_{18}N_3SCl)_2,ZnCl_2,H_2O$. It appears as dark green crystals with a bronze luster soluble in water, alcohol and chloroform. The U.S.P. grade has varied medicinal uses.

Sugar coloring or **caramel** is a dark-colored semisolid mass. It can be prepared by the careful heating of sucrose, glucose or molasses, usually to about 170-180° C. in the presence of a dilute alkali such as ammonium hydroxide. Commercially it is usually made from glucose. It is used as a brown coloring agent for foods, liquors and beverages. Varied types are available such as alcohol-stable, acid-stable, etc.

Walnut-brown crystals consist of finely ground peat or decayed vegetable matter. The product owes its name to color, not origin. It is imported from Germany. This water-soluble material is used as a stain for wood and in coloring ordinary wrapping paper.

CHAPTER XXIX

TONERS, LAKES AND REDUCED COLORS

Those familiar with the pigment industry are accustomed to divide color materials into three general classifications: (1) **Toners** are pure color agents containing no inert matter. They may be either organic or inorganic. (2) **Lakes** contain an active color agent plus inactive material. They are made by precipitating the color agent on an inert base such as barium sulfate or aluminum hydroxide, each of which is an insoluble white material. By this method of preparation the individual particles of inert material are coated with the color agent, so that examination under the microscope would show an apparently homogeneous product. (3) **Reduced colors** are similar in composition to lakes but are prepared differently. They are a dry blend of toner with inert material made by mixing the two ingredients in the dry state. They show their heterogeneity when examined under the microscope. Reduced colors get their name from the fact that the concentration of color agent has been reduced by the addition of an inert substance.

It will be seen from the above that toners are used alone and in the preparation of lakes and reduced colors. The names under which these materials are sold are innumerable. As with dyes, the same material may be sold under a dozen different names by as many different companies. Also names are used which may stand for a particular product in one company, but which may represent a general classification in another company covering thirty or more different products, each differing from the other in the final color effect. For example, one firm might quote a price on Rose Lake, which would be a particular product which they chose to sell under that name. To another company such a designation might have no meaning at all, as they might offer a whole line of products that could be described as rose lakes.

While a dye is a soluble compound, and is applied dissolved in a suitable solvent to fabric or other material, a pigment is insoluble, and imparts color to objects by application in the form of finely divided particles suspended in a suitable liquid vehicle.

Dispersed color, formerly called **flush color,** is a classification covering many products. It refers to the state in which the color agent is sold, rather than to the individual color. Dispersed color is never dried and ground but appears on the market in the form of a heavy paste, or **pulp color.** The water in the pulp may be replaced by a number of vehicles such as alkyd resins, linseed oil, lithovarnish, ester gum, castor oil, etc. The method of manufacture preserves the original small particle size of the color agent. This gives it greater brilliance, greater color strength, and in some cases improved light fastness. Dispersed colors are used in paints, lacquers and printing inks. This classification applies to many colors covered in previous chapters.

Phosphotungstic pigments are lakes and toners produced by precipitation of the dyestuff from aqueous phosphate and tungstate solution by addition of mineral acid. The possible formulas are too diverse to quote here. Their properties are great brilliance and permanence. In some cases part of the tungstate is replaced by molybdate. These pigments are of relatively recent development.

Iron-base lakes consist of dyestuffs precipitated on iron oxide. Because the base as well as the dyestuff is part of the color, in many cases these are discussed under iron oxides rather than in this chapter. An example is that of Tuscan red.

Alizarin-red lake is made from alizarin, which was formerly obtained from a glucoside occurring naturally in madder root. It is now made from anthracene by oxidation to anthraquinone, sulfonation of the latter, and fusion with sodium hydroxide to give 1,2-dihydroxyanthraquinone. The soluble sodium salt of alizarin or the dye, in the form of orange-red crystals, is then reacted with a solution of an aluminum or tin salt, which gives the insoluble alizarin red lake. Other metals give other colored lakes. Alizarin-red lake is used as a pigment in paints, artists' colors, and inks.

Eosin red is prepared from brominated fluorescein. It is a brownish red powder, the disodium salt of tetrabromofluorescein. The dye is easily soluble in water, somewhat soluble in alcohol. Dilute aqueous solutions show a yellow-red fluorescence, alcoholic a yellow-green. The dye is used for coloring ink, fabric, straw, paper, and cosmetics, as a stain in microscopy, and for the preparation of pink lakes. These are quoted as blue-shade toner and yellow-shade toner.

Para toner is a general name covering a number of insoluble red color agents. These are based on a combination of *p*-nitroaniline and β-naphthol. The latter may be replaced in part by mono acid F, 2-naphthol-7-sulfonic acid. The different shades of red are obtained by varying the conditions under which the color is struck, such as the temperature and pH of the medium. Para toners are used as pigments in the paint trade, to some extent in the printing industry, and in making para lakes.

Toluidin toner is a red organic color agent produced by the combination of *m*-nitro-*p*-toluidin and β-naphthol. It is used in paints, lacquers and printing inks.

Scarlet-ink lake is a red lake made by precipitating the dye Scarlet 2 RR on an inert base such as aluminum hydroxide or barium sulfate. The dye itself is formed by the combination of xylidine and the disodium salt of 1-naphthol-3,6-disulfonic acid. The lake is used in inks and is ground directly into the ink from the pulp. It is marketed in this form, as the color agent cannot be dried without losing practically all of its strength. **Scarlet-ink toner** is the lead salt of the dye, Scarlet 2 RR and is used in inks.

Lake-red C toner is the derivative formed by combining *p*-chloro-*m*-toluidin-*o*-sulfonic acid and β-naphthol. It is used in printing inks and to a small extent in lacquers.

Lithol toner is a red pigment made from Tobias acid, 2-naphthylamine-1-sulfonic acid, and β-naphthol. It is used principally in printing inks and to a lesser extent in the paint trade.

Lithol-rubin toner is a red pigment consisting of the calcium and strontium salts of β-hydroxynaphthoic acid. It is used in printing inks and in paints.

Phosphotungstic rhodamine-Y red is a red pigment consisting of the tungsten derivative of a synthetic dye of the xanthene class. Phosphotungstic acid is used as the source of tungsten. The pigment is very expensive and is used in printing inks.

American vermilion is a red pigment prepared from basic lead chromate, chrome red, barium or lead sulfate and aluminum hydroxide, with the addition of a para toner or a red dye such as eosin, to increase saturation. It is used in paints.

Maroon red lake is usually that of amaranth, often quoted at 25 per cent strength.

Carmine red or **carmine** is a lake produced from cochineal. It is the precipitate of the aluminum salt of carminic acid obtained by treatment of the cochineal with water to extract the acid, and subsequent precipitation with aluminum salts. It is insoluble in water and used as an expensive pigment.

Red rose lake is a lake pigment prepared by the combination of diazotized 2-naphthylamine-4-sulfonic acid and an alkaline solution of β-naphthol-3,6-disulfonic acid. The dye is precipitated on a barium sulfate base. It is used in printing inks. **Pink rose lake** is a more dilute form of rose lake.

Orange lake is a term for several oranges, such as **para orange.** These are closely related to the para reds. **Persian orange lake** is an organic orange pigment prepared from 2,4-dinitroaniline and β-naphthol. It is used in paints and printing inks.

Orange toners are a general class of dyestuffs. They are usually diazo compounds that contain no sulfonic or carboxylic groups but which are coupled with diacetoacetic acid arylides. They are used in printing inks.

Dutch yellow or **Dutch pink** is a yellow lake prepared by absorbing the yellow dye of oak bark, quercitron, on an inert material such as Paris white, calcium carbonate, or a similar base. It is used as an artists' pigment, as a pulp color for wall paper, and to tone Brunswick Green.

Tungsten lakes are derivatives of some of the brilliant but fugitive basic dyes, formed to make the latter permanent as well as brilliant. The tungsten products are more costly but will stand considerable reduction. The more important of the basic dyestuffs which lend themselves to this method of treatment are brilliant green, malachite green, Victoria green, methyl violet, Victoria blue, rhodamine 6G, rhodamine B, setoglaucine or its equivalent, and magenta. Examples of the commercial products are **tungstated brilliant green, tungstated emerald green, tungstated peacock blue,** and **tungstated Victoria blue.** Peacock blue is a pigment derived from the acid dyestuff erioglaucine, which is a complex sulfonated derivative of triphenylmethane. The dyestuffs are generally the water-soluble hydrochlorides of the dye bases. These are dissolved and usually diluted to about 1 per cent, then precipitated by adding the required amount of the complex acid salt of tungsten. The manufacturer usually purchases sodium tungstate and makes up a solution by dissolving in water, along with some disodium phosphate, then acidifying the solution with a definite amount of hydrochloric acid. The treated dye is precipitated and further processed as usual. The tungstated dyes are used in printing inks.

Alkali blue toner belongs in the triphenylmethane class. It is a sulfonate of sodium triphenyl-*p*-rosaniline. The extent of sulfonation is variable and is the means by which the shade of blue is controlled. The pigment is used in printing inks.

Victoria blue ink toner is the tungsten derivative of Victoria blue, a triphenylmethane dye, dispersed in lithovarnish. It is used in printing inks.

Methyl violet toner and **permanent methyl violet** are tannated methyl violet dyes ground in lithovarnish and used as base inks.

Purple lakes are produced by combining compounds such as 2-diazo-naphthalene-1-sulfonic acid, and β-hydroxy-naphthoic acid. Numerous combinations are possible, and cover such general names as maroon lakes and **purple lake red.** **Purple lake toner** refers to this type of dyestuff. The lakes are used in printing inks. A particular example is known as **purple lake 3B.**

CHAPTER XXX

NATURAL PLANT PRODUCTS

Natural plant products are produced in the vegetable kingdom as a physical part of plant life. They are always complex materials and therefore defy simple chemical classification. Parts or the whole of vegetable organisms such as herbs, roots, barks, flowers, fruits, seeds, leaves, etc., in great number have been utilized in industry. Many of them are used in medicine for their physiological effect. The subject is necessarily interpreted broadly to include fungus growths and even one insect, used medically. The products listed are as found in nature, subjected merely to the simple processes of cleaning and drying, separating from contaminating materials, possibly powdering, and in some cases bleaching. Because of the large number of such items and their relatively minor importance they are each discussed only briefly. When physiological properties are referred to, see Appendix B for interpretation of the medical terms used. If not U.S.P., those having medical properties are usually N.F. products, occasionally B.P.C. or French codex. Where in U.S.P.XI they are referred to as U.S.P., but if in U.S.P.X but not in U.S.P.XI the edition is stated. In general each type such as roots, leaves, etc., have been grouped together. Such classification is necessarily not complete, since frequently two forms of the same plant or tree are sold. The classification which predominates of medicinals, includes most of the commercial spices and many sources of tanning materials. This necessarily leads to subclassification which cuts across grouping of barks, roots, etc. Many of the materials have numerous names. The common industrial name has been used. The botanical name given often corresponds to a medical term which has not been repeated. The botanical name has been shortened as much as feasible for identification. For listing of special names not given here, it is suggested that the reader refer to Mercks' Index, or to an unabridged dictionary, which go into greater detail of that kind.

It is to be borne in mind that cellulose, tannin, resins and gums are widely distributed in plant products. Often their presence is not mentioned because the content is only normal.

The **coffee** bean is a natural product obtained from trees and shrubs of the family *Coffea arabica,* which grow in tropical countries, particularly in Brazil, the West Indies, Africa and India. A crude treatment is simply to gather the coffee berries and let them dry in the sun, later removing the dried parchment and pulp from the inner berry. The more modern wet method is to soak the berries in water, loosen the pulp by friction, float the pulp off and collect the separated seeds. The berries are then dried and the parchment and silver skin broken and removed by winnowing. The berries are graded by size and are then ready for roasting.

The roasting process is very important as it liberates caffeine from caffetannic acid and also develops the aromatic principle. Unsatisfactory results are obtained if the roasting is not accurately controlled. A certain degree of freedom is permissible, according to the tastes of the users in certain sections, so that grades such as cinnamon, city, medium and dark, are prepared. Dark coffee beans are the result of a high roast, which means that a relatively large amount of heat has been applied.

Coffee is sometimes adulterated with cereal grains and other seeds. Addition of chicory may or may not be considered adulteration, as in some countries the added chicory flavor is preferred to that of straight coffee.

To get the best infusion of coffee as a beverage, the beans should be available when freshly roasted and also freshly ground to the correct size. Since ground coffee is largely in demand in the retail market, various attempts have been made to insure the coffee reaching the consumer when freshly ground. One of these is to mark on the label the date when the coffee was ground, and to supply this only as needed by the grocer. Vacuum-packed coffee is sold extensively. The theory is that if packed in a high vacuum, the absence of any appreciable amount of oxygen will arrest the aging and associated deterioration of the coffee. This seems to be partly true. However, changes do occur in the vacuum-packed can of coffee, notably liberation of absorbed carbon dioxide, which explains the pressure of gases built up in the vacuum-packed can. A large amount of research continues to be conducted with a view to improving the quality of the coffee as it reaches the ultimate consumer.

Grades commonly quoted include Santos, Santos peaberry, Rio, Bucaramanga, Bogota, Bogata peaberry, Maracaibo, Guatamala, Mocha, Java, Robusta, Mexican, Haiti, Costo Rica, East Indian, etc. A powdered extract prepared *in vacuo* is available, as well as liquid concentrated extracts.

Chicory root is obtained from a plant, *Cichorium intybus,* widely cultivated in Europe. The roots are roasted and ground for admixture with coffee. In this country this is usually considered to be adulteration, but in many European countries chicory is considered to improve the flavor and quality of coffee. Chicory increases the color and body of coffee, in addition to giving it a somewhat bitter taste and frequently sells for a higher price than many grades of coffee.

Tea leaves are a natural product obtained from bushes of the family, *Thea sinensis,* cultivated in China, India, Ceylon and the Dutch East Indies. Two different kinds are obtained, black tea and green tea, which are the result of the method of treatment of the leaf.

Black tea is produced by first spreading the gathered leaves in a thin layer in a withering house, where they become soft and flexible. They next pass through a rolling machine which breaks up the cell walls so that the inner juices are liberated and consequently will ferment more readily, and which also gives the leaves their rolled shape. They are then spread out in moist rooms to induce the growth of oxidative enzymes which cause the necessary changes for full development of the characteristic flavor. During this stage quantities of yeast cells are produced. These seem to be closely associated with the development of aroma and taste. At the same time some of the tannin is broken down into yellow and brown colored products. This accounts for the difference in color between black tea infusions and green tea infusions and also for the lesser content of tannins in black tea. The leaves are next fired to kill enzymes and to dry the leaves. After this they are graded by the size of the leaf. The graded tea is stored, again dried, and packed, usually in lead-lined boxes. Grades are Orange Pekoe,

Pekoe, Pekoe Souchong and Souchong, the first grade representing the youngest and best leaves.

In the preparation of green tea it is necessary to avoid fermentation. The gathered leaves are therefore subjected immediately to a heat treatment to kill enzymes. The leaves are then centrifuged to remove liquids, rolled lightly, fired, graded and packed as in the case of black tea. Both kinds of tea are kept in air-tight containers during storage and when packed, to preserve their delicate aroma. Grades commonly quoted include Formosa, China greens, Japan basketfired, Japan panfired, Young Hyson, Sumatra, Java, Congote, India Orange Pekoe, Ceylon Orange Pekoe, Java Orange Pekoe, etc., each often with subgrades.

Mustard seed is the seed of varieties of mustard plant which grow in various parts of the world. **Black mustard** or **brown mustard** is the dried ripe seed of *Brassica nigra, Brassica juncea* or related species which grow in Europe, Asia and the United States. The U.S.P. permits not more than 5 per cent of other seeds or other foreign organic matter. Not less than 0.6 per cent of volatile oil of mustard must be present. The seed contains allyl isothiocyanate. Medically it is a carminative and local irritant. It is the source of oil of mustard. **White mustard** or **yellow mustard** is the ripe seeds of *Sinapis alba* growing in the same regions. It has similar medical uses. Mustard is sold according to the origin, as the yellow or brown grade. Brown grades come from Bombay and California, yellow grades from California, China, Denmark, Holland, England, Hungaria and Rumania. Both grades are used as a condiment.

Turmeric root, curcuma or **Indian saffron** is the dried rhizomes of *Curcuma longa,* native to China, the East Indies and many tropical countries. It contains a yellow coloring matter curcumin, starch, resin and about 5 per cent of an essential oil. Alleppey and Madras grades are sold. It is used medically as a tonic and hepatic stimulant. Industrial uses are as a condiment in food, as a source of curcumin and as a coloring matter.

Ginger root consists of the dried rhizomes of *Zingiber officinale* with the outer cortical layers removed. In commerce *this is known as* **Jamaica ginger.** *It must contain at least 4.5 per cent of ether-soluble extractives to meet the U.S.P. standards. Ginger is grown in all tropical countries.* There is 0.25 to 3 per cent of volatile oil present with an acrid resin and gingerol. Typical grades are African lemon Cochin, bold medium Jamaica, bright grinding Jamaica, and Japanese. The ground root is used as a condiment and in medicine as a stimulant, counterirritant, carminative, rubefacient, stomachic, digestive, sternutic and sialagogue.

Cinnamon or **Ceylon cinnamon** is the dried inner bark of cultivated *Cinnamomum zeylanicum,* grown throughout tropical countries. It contains 1-2 per cent of volatile oils, cinnamic aldehyde, tannin, sugar, etc. The price tends to be about double the average for cassia. Medically it is an astringent, carminative, stimulant and stomachic. Its most important uses are industrial, as a source of oil and as a condiment.

Taigon cinnamon is similarly derived from *Cinnamomum loureirii.* It is the U.S.P. grade and must contain not less than 2 per cent of volatile ether-soluble extractive and not more than 2 per cent of foreign organic matter. Its uses are similar to those of Ceylon cinnamon.

Cassia or **Chinese cinnamon** is a term applied to the shrub or tree of several varieties. In the trade it is a coarse cinnamon bark from *Cinnamomum cassia* and a related species. It contains 1-2 per cent of volatile oil, sugar, tannins, gums and coloring matter. The habitat is Southern China, Cochin China, and Eastern Asia. It is a carminative and astringent. This enters the market as grades 1,2 and 3 for the Batavia grade, rolls and broken for the China grade, and as Saigon. The latter is the best, China grades are poor. All are much cheaper than true cinnamon and are used for similar purposes and flavors. **Cassia buds** are the dried unripe fruit of various species of *cinnamomum.* The buds resemble cloves but are smaller. They contain 1-2 per cent of volatile oil, with tannins, and are used as flavors, being less expensive than cinnamon.

Canella alba bark, white cinnamon or **wild cinnamon** is the inner orange-colored and highly aromatic bark of the *Canella alba,* a tree which grows in southern Florida and the West

Indies. It contains about 1 per cent of a volatile oil in which eugenol, cineol and terpenes are present. Mannite and resin are also present. It is used as an aromatic and stomachic, as a tonic and as a condiment.

Nutmeg is the dried ripe seed of *Myristica fragrans* deprived of its seed coat and arillode, with or without a thin coating of lime. The tree is native to the Molucca Islands and cultivated in the East and West Indies and Brazil. In addition to 25-40 per cent of fixed oil some 5-15 per cent of volatile oils are present. Grades sold are 75-80 to the pound, 105-110 to the pound, and West Indian. It is sold whole and ground as a spice, and is the source of nutmeg oil. The U.S.P. standard requires not less than 25 per cent of nonvolatile ether-soluble material and not more than 0.5 per cent of acid-soluble ash. Medically it is a carminative and digestive.

Mace is the highly aromatic external fibrous covering of nutmeg seeds obtained from *Myristica fragrans*, imported from Banda, Batavia and several tropical countries. It contains 5-15 per cent of volatile oil with resin, gums, etc. Medically it is a carminative, tonic and stimulant. The major use is industrially as a spice.

Pepper is the dried fruit of *Piper nigrum*. **Black pepper** consists of the dried unripe berries; **white pepper** of the dried ripe seeds freed of their natural coating. These are grown in tropical Asiatic areas. **Red pepper, Cayenne pepper, capsicum** or **chillies** are the dried pods of *Capsicum frutescens,* also grown in the tropics. They contain 1-2.5 per cent of volatile oil and 5-8 per cent of piperine with piperidine, fat, resin, etc. Pepper is used mainly as a condiment. Grades of black pepper are Lampong, Aleppy, Tellicherry, etc. White pepper is largely from Java. Black and white pepper are used in medicine as a carminative, stimulant, antipyretic, irritant, tonic, rubefacient and febrifuge. Red pepper has similar properties in proper proportions. The U.S.P. grade of cayenne pepper contains not more than 3 per cent of stems and calyxes, not more than 1 per cent of other foreign organic matter, not less than 12 per cent of nonvolatile, ether-soluble extractive, and not more than 1.25 per cent of acid-insoluble ash.

Paprika is the dried red ripe fruit of the bonnet pepper, *Capsicum tetragonum.* Grades of Hungarian and Spanish paprika are extra fancy, fancy, medium and fair. Paprika is ground and used as a mild spice.

Cloves are the dried flower-buds of a widely cultivated tree, *caryophyllus aromaticus,* grown in many areas. According to U.S.P. standards not more than 5 per cent of stems nor 1 per cent of other foreign organic matter is permitted. They contain not less than 15 per cent of volatile ether-soluble matter and not more than 10 per cent of crude fiber nor more than 0.75 per cent of acid-soluble ash. The volatile oil is largely eugenol. Madagascar and Zanzibar grades are offered. They are used as carminative, stomachic, and antiemetic. Their important use is industrial, as a flavor in cooking, as a source of eugenol and for the production of flavorings.

Pimento or **allspice** is the dried, nearly ripe fruit of *Pimenta officinalis.* It contains 3-5 per cent of volatile oil with resins, gums, etc. Pimento is medically a carminative, stimulant and stomachic. Industrially it is a condiment.

Anise or **aniseed** is the dried ripe fruit of *Pimpinella anisum,* an herb which grows in Egypt and western Asia and is cultivated in many parts of the world. The seed contains 1.5-3.5 per cent of volatile oil. Spanish, Russian, Italian and Star grades of anise seed are sold. Medically it is a carminative, stimulant, stomachic, expectorant and aromatic. It is important industrially as a flavor for foods and liquors, as a condiment, and as the source of anise oil.

Sarsaparilla root is the dried root of various species of *Smilax* which grow in Mexico, Central and South America, known in commerce as **Mexican sarsaparilla, Honduras sarsaparilla, Central American sarsaparilla** and **Jamaica sarsaparilla.** According to U.S.P. standard is must not contain more than 2 per cent of organic matter foreign to the rhizome and crown. Mexican sarsaparilla contains not more than 10 per cent of rhizome and stem portion and not more than 4 per cent of acid-insoluble ash. The others are limited to 2 per cent of acid-insoluble ash. It is imported from Mexico and Honduras, the latter being about twice as expensive as the former. A powdered extract of the Mexican root, prepared *in vacuo*, is sold. The root serves to produce an infusion used in flavoring, especially in soft drinks, and in medicine as a mild tonic alterative, diuretic, diaphoretic and antisyphiletic.

Sassafras bark is the bark from the roots of a North American tree, *Sassafras variifolium*, of the laurel family. The bark contains 6-9 per cent of volatile oil, together with tannins, resins, gum and wax. It is sold as ordinary and select grades. Sassafras is an aromatic, diaphoretic, stimulant, alterative, astringent, and diuretic. It is the source of the sassafras oil used in flavors and perfumes. **Sassafras root**, containing about 2 per cent of oil, is also sold.

Angelica root is from a biennial herb, *Angelica archangelica* which grows in Europe and Asia. It contains up to 1 per cent of volatile oil with resin, starch, etc. Grades sold are domestic and imported, natural and twisted. It is used for the production of angelica-root oil, as a flavoring in candy and food and in medicine as an aromatic, carminative, diaphoretic, stimulant and nervine. **Angelica fruit** has quite similar properties.

Witch-hazel leaves are the dried leaves of *Hamamelis virginiana*, a shrub native to North America. They are collected in the autumn, and are an astringent and tonic. **Witch-hazel bark** and twigs are also sold. Both are used as a source for distillation of the volatile oil present in witch hazel extract. A powdered extract, prepared *in vacuo* from the leaves, is sold.

Vanilla beans are the cured full-grown but unripe fruit of a tropical American plant, *Vanilla planifolia*. They contain from 2-3 per cent of a fragrant, pleasant-tasting crystalline compound, vanillin, together with about 4 per cent of resins and much sugar. The commercial beans are often covered with a natural coating of vanillin crystals. Grades of the beans sold are Bourbon, Mexican and South American, packed in tins. Both whole and cut beans are sold, the latter in a form for extraction. Medically they are an aromatic, antihysteric, antirheumatic, aphrodisiac and emmenagogue. Industrially they are the source of true **vanilla extract** by extraction with dilute alcohol. Vanilla beans are ground, and introduced into ice cream. In some countries the whole beans are a confection.

They are used in the preparation of perfumes. While synthetic vanillin is available, the artificial vanilla extract so prepared lacks some of the resins and other ingredients of the natural bean and the flavor therefore does not match the natural vanilla flavor.

Tonka beans, or **Coumarouna beans** are obtained from a tropical South American tree, *Dipteryx oppositiafolia.* They have a pleasant odor because of the presence of up to 3 per cent of coumarin. A commercial source is Angostura in Venezuela. They are medically an antispasmodic, narcotic and stimulant. Industrially they are used in the manufacture of imitation vanilla flavors, in perfumes and in flavoring tobacco. Synthetic coumarin has rendered them less important in vanilla flavors than they formerly were.

Spearmint consists of the dried leaves and tops of *Mentha spicata,* common garden mint, growing over a widespread area. The U.S.P. standard requires not more than 2 per cent of stems over 3 mm. in diameter and no foreign organic matter. They are high in volatile oil and are used as a source of that oil, as a flavor and as a carminative.

Peppermint consists of the dried leaves and tops of *Mentha piperita,* which grows in Europe, Asia and North America. The U.S.P. standard requires not more than 2 per cent of stems over 3 mm. in diameter, or other foreign organic matter. Both imported and domestic grades are quoted, the imported being more expensive. It is used as a source of an essential oil, as a flavoring material, and in medicine as an aromatic, stimulant, carminative, nervine and antispasmodic.

Wild cherry bark is the stem bark obtained from the uncultivated wild black cherry or chokecherry tree, *Prunus serotina.* It must be collected in the autumn and carefully dried to meet the U.S.P. standard. It contains various tannins, emulsin, benzoic acid, resin, etc. Grades sold are thick, natural and rossed, and thin, natural and rossed green. A solid extract prepared *in vacuo* is available. It is used as a tonic, febrifuge and sedative. Technical uses are as bitter flavoring material.

Wormwood is the dried leaves and flowering tops of an herb, *Artemesia absinthium* grown in Asia, Africa and the United

States. It contains a bitter glucoside absinthin, volatile oil, succinic acid and tannins. It is used as febrifuge, anthelmintic, tonic, stimulant and stomachic. Either the fresh or dried herb may be used to produce oil of wormwood of varying qualities. The herb is extracted as a flavor for alcoholic beverages.

Juniper berries are the dried, ripe fruit of a shrub *Juniperus communis,* growing in Europe, Asia and North America. They contain considerable amounts of volatile oil, which varies substantially in constants according to where they are grown. A powdered extract prepared *in vacuo* is available. Medically the berries are a diuretic, anodyne, emmenagogue, stimulant, stomachic and carminative. Industrially they are the source of an essential oil and an essential ingredient of the flavor of some liquors, particularly gin.

Coriander seed is the dried ripe fruit of *Coriandrum sativum* grown in Asia and Europe. The Moroccan seed is sold bleached and unbleached. Russian coriander seed is also sold. It is used as a seasoning and flavor for foods and beverages. Medically it is a stimulant, aromatic and carminative.

Cardomom seed is, according to U.S.P. standards, the dried ripe seed of an East Indian herb, *Elettaria cardamomum,* recently removed from the capsules, and must not contain more than 5 per cent of acid-soluble ash. It contains 2-8 per cent of oils along with resins, etc. Commercial grades are bleached, decorticated and green. The seed is used as a condiment, in flavoring alcoholic beverages, and in medicine as a stimulant, stomachic and carminative.

Calamus root or **sweetflag** is the dried rhizome of *Acorus calamus,* native in Europe, North America and Western Asia and cultivated in Burma and Ceylon. It contains 1.5-3.5 per cent of volatile oil with resins, starch and tannins. Calamus is used as a flavoring for gin and other beverages, and in medicine as a tonic, stomachic, carminative, stimulant and bitter principal. A bleached grade is sold as well as the peeled root, the latter being relatively inexpensive.

Caraway seed is the dried ripe seed, the fruit of *Carum carvi,* an aromatic herb which grows in various parts of the world, and is imported into this country from Holland. According to

U.S.P. standards, it must not contain more than 3 per cent of other seeds or foreign organic matter, nor more than 1.5 per cent of acid-soluble ash. It contains 3-7 per cent of volatile oil, along with resin, sugar, tannin and gums. Caraway is used as a condiment in food and confectionery, as a flavoring for liqueurs, and in medicine as a stimulant, diuretic, stomachic and carminative.

Sloe berries are the dried ripe fruit of a blackthorn, *Prunus spinosa.* They resemble huckleberries and are used for flavoring sloe gin. **Dried raspberries** are the dried ripe fruit of plants of the genus *Rubus* grown in the north temperate zone. Aside from flavoring materials they are high in organic acids. Uses are mainly as flavoring substances.

Bitter orange peel is the dried outer rind of unripe *Citrus aurantium* by U.S.P. definition. **Sweet orange peel** is by the same definition the fresh outer rind of ripe *Citrus aurantium sinensis* which has not been artificially colored. Commercially, bitter orange peel is usually from the Curacao or Seville oranges, *Citrus vulgaris,*—and sweet orange peel, the dried peel from the sweet orange specified by U.S.P. Both types are widely grown. Both are high in oil content. Powdered extracts of each, prepared *in vacuo,* are sold. Bitter orange peel is a carminative, tonic, stimulant and stomachic. Both yield an orange oil, but only sweet orange oil is commonly used. The peels are used in producing flavors in foods and liquors.

Lemon peel is the dried outer rind of ripe lemons, *Citrus medica limonum,* which grow in various parts of the world in semitropical climates. The U.S.P. product must be obtained from fresh ripe fruit. It is used as a tonic, refrigerant, antiscorbutic and corrigent. Lemon peel is a source of lemon oil and is used in foods, confectionery and liquors. A powdered extract prepared *in vacuo* is also sold.

Licorice root is the dried rhizomes and roots of varieties of *Glycyrrhiza glabra,* yielding a yellow sweet wood such as are known in commerce as Spanish licorice, Russian licorice, etc. Not more than 2.5 per cent of acid-insoluble ash is permitted by U.S.P. standards. It is grown in Southern Europe, Central Asia and the United States and contains 2-7 per cent of licorice, about 1.25 per cent of asparagin, glucose, sucrose, resin, etc. Ordinary and select root, largely imported from Europe, are sold, as well as powdered root and a solid extract of the root prepared *in vacuo*. The selected root is relatively expensive. It is an expectorant, corrigent, slight stimulant, demulcent and laxative, and is largely used to cover flavors of other medicinals. Industrially it is used largely as a source of the extract.

Hops are the carefully dried, cone-shaped flowers obtained from a widely cultivated climbing vine, *Humulus lupulus*. They contain about 0.3 per cent of volatile oil with hard and soft resins, tannins, etc. Both domestic and imported grades are sold, the imported being more expensive. A powdered extract prepared *in vacuo* is also sold. Medically they are a carminative, diaphoretic, hypnotic, sedative, anodyne, diuretic, antispasmodic and tonic. Industrially they are much more important as used in the production of malt beverages such as beer.

Marjoram or **sweet marjoram** is a widely cultivated European and Asiatic herb, *Origanum majorana*. It is imported from France and Tunis. Marjoram is used in medicine as a tonic, diaphoretic and emmenagogue, and industrially as a condiment.

Saffron flowers are the stigmas of *Crocus sativus*, widely cultivated in Southern Europe and Asia. They contain a glucoside, oils, wax, etc. Medically they serve as emmenagogue, antispasmodic, antihysteric, diaphoretic, anodyne, and stomachic. Grades sold are American, Mexican and Spanish. They are used principally as a source of a natural orange dye to color food and also impart some flavor.

Fenugreek seed is the seed of *Trigonella foenum-graecum*, a leguminous plant cultivated in France, Germany, Egypt and Asia Minor. Some 6 per cent of oil is present. It is used medically in poultices, and as an artificial maple flavoring for foods. A powdered extract prepared *in vacuo* is available.

Grains of paradise are the pungent seeds of a West African plant, *Amomum melegueta*. They contain about 0.25 per cent of volatile oil and are used as a condiment and in veterinary medicine.

Fennel seed is the dried ripe fruit of cultivated varieties of *Foeniculum vulgare,* grown largely in Europe and western Asia. It contains 4-5 per cent of volatile oils. French and German seeds are imported, the latter in large and small grades. The seed is used in medicine as a stimulant, expectorant, carminative, galactagogue and stomachic. Fennel is also used as a flavor in foods.

Dillseed is the dried ripe fruit of *Anethum graveolens,* the garden dill. It is cultivated in Europe and the United States and contains 3-4 per cent of volatile oil. Dillseed is sold as dewhiskered, polished and recleaned. Uses are as a condiment, especially for pickles, for extraction of dill oil, and as a galactagogue, carminative, stimulant and stomachic.

Celery seed is the dried ripe seed of *Apium graveolens,* cultivated in nearly all parts of the world. It is imported from France and India, and is used as a condiment. In medicine it serves as a sedative, diuretic and febrifuge. A powdered extract prepared *in vacuo* is available. **Celery root** is used somewhat similarly in medicine.

Sage or **salvia** is the dried leaves of a shrub, *Salvia officinalis* which grows in this country and Europe. They contain 1-3 per cent of volatile oil with the usual resins, gums, and tannins. Dalmatian sage leaves are imported and quoted as stemless. Garden sage is also available. They are a tonic, astringent and stimulant but are mainly used as a condiment.

Thyme consists of the dried leaves and flowering tops of a pungent aromatic plant, *Thymus vulgaris,* native to Southern Europe but cultivated in various parts of the world. They contain volatile oil, tannins and gums. Thyme is imported from France and Spain for use as a seasoning agent in food. It is also used as antipyretic, carminative, antiseptic and antispasmodic.

Savory or **summer savory** consists of the dried leaves of an aromatic mint, *Satureia hortensis,* grown in Europe and the United States. It is used in medicine as a stimulant, carminative and emmenagogue. The major use is as a condiment.

Horehound or **hoarhound** consists of the dried leaves and tops of *Marrubium vulgare.* This grows in Europe, Asia and the

United States, and is a kind of mint. It is used as a stimulant, resolvent, tonic, diaphoretic, laxative, vermifuge and nervine. Horehound is also used in cough medicine and in confectionery. A powdered extract prepared *in vacuo* is available.

Manna is the dried exudate from *Fraxinus ornus,* a variety of European flowering ash. The U.S.P. X standard requires not less than 75 per cent of alcohol-soluble extractive on an anhydrous basis by extraction with 90 per cent alcohol. The commercial form is as large and small flakes, of which the large are much more expensive. It contains 40-60 per cent of mannite or mannitol and is very soluble in water. Medically it is a cholagogue, expectorant, nutrient, demulcent and laxative. Industrially it is a source of mannite or mannitol.

Pyrethrum flowers or **insect flowers** are obtained from *Chrysanthemum cinerarifolium* grown in Asia, Africa, Dalmatia and Japan. They contain about 1-1.5 per cent of volatile oil in which pyrethrins are present. Grades sold are coarse and finely ground Dalmatian and Japanese flowers. The latter are the main supply. They are used in powdered form as insecticides and for extraction to produce liquid insecticides, usually on the basis of pyrethrin content.

Derris root is from *Deguelia elliptica,* a plant grown in Europe and the East Indies. It contains rotenone, tubatoxin and acid resins poisonous to lower forms of animals but relatively nonpoisonous to humans. It is sold in bales and powdered, the latter as 4 per cent and 5 per cent rotenone, at prices based on the rotenone content. Use is in the manufacture of insecticides.

Cubé root is obtained from several tropical American plants of the genus *Jacquinia.* The dried powdered product is used in the manufacture of insecticides. Cubé root was used originally as a fish poison because it is not poisonous to humans. Commercially it is used for its rotenone content and is so quoted, as powdered and coarse, with 5 per cent, 4 per cent and 3 per cent content of rotenone.

Timbo root is the root of a South American woody vine, *Paullinia pinnata.* The root is imported in powdered form, sold on the basis of its rotenone content as 5 per cent and 4 per cent grades and used in preparation of insecticides.

White hellebore and **black hellebore** root consists of the dried rhizomes of the genus *Helleborus.* The black variety is a cathartic, tonic, hydragogue and emmenagogue. The white variety is an emetic, diaphoretic, errhine, sternutic and antipyretic. The white variety is powdered and used externally for its insecticidal value. Powdered concentrates prepared *in vacuo* are available.

Green hellebore consists of the dried rhizomes and roots of *Veratrum viride.* It is required by U.S.P. grading to contain not more than 5 per cent of stems or other foreign organic matter and not more than 4 per cent of acid-insoluble ash. It is a sedative, emetic, diaphoretic, irritant, sternutic, errhine and diuretic.

White squill is a U.S.P. product consisting of the cut and dried fleshy inner scale of the bulb of the white variety of *Urginea maritima, Scilla* or **sea onion.** It grows wild in pear-shaped bulbs weighing 2-4 pounds, in southern Europe, northern Africa and Asia, and is sold in coarse and powder form. White squill contains several glucosides and is used in medicine as a heart stimulant, diuretic, cathartic, emetic and expectorant. A powdered extract and a stronger concentrate, both prepared *in vacuo,* are available. **Red squill** is quite similar and not distinguished botanically. It may also be from *Urginea burkei.* Red squill is sun-dried or preferably oven-dried and is used as a rat poison. The active ingredients are glucosides. It is relatively nontoxic to humans, domestic animals and fowls. An extract is also sold under trade names.

Stavesacre seed, or **Staphisagria,** is the ripe seed of *Delphinium staphisagria,* the **Eurasian larkspur.** The seeds contain several alkaloids, the principal one being delphinine. Medically they are an emetic, rubefacient, antineuralgic, diuretic and cathartic, and are in U.S.P. IX. Industrially they are the source of delphinine and are used in insecticides, particularly against mites.

Sabadilla seed are the seeds of *Schoenocaulon officinalis,* a plant which grows in Mexico and Central America. The usual commercial grade is powdered. It is used in medicine as a cathartic, emetic and vermifuge. Industrially it is used in insecticides against lice and as a source of the alkaloid veratrine.

Red saunders wood, red sandalwood or **ruby wood** is the heartwood, of *Pterocarpus santalinus*, an East Indian tree. There is a U.S.P. standard for the product. The ground wood is an astringent and tonic but is used primarily as a source of a natural dye. Other uses are as an odorant and in cosmetic products.

Camwood is the red heartwood of an African tree, *Baphia nitida*, sold in ground form. The extract is used as a dye. Confusion with the term **barwood** sometimes arises but they are probably identical. **Camwood bark** is the hard red bark from the same tree. It is used for extraction of dyestuff.

Wattle bark is obtained from various Australian, Indian and African trees or shrubs of the genus *Acacia*. The bark contains 25-35 per cent of tannin. Gallic acid is also present. The bark is used for preparation of tanning extract.

Mangrove bark is obtained from *Rhizophora mangle*, the mangrove tree. Sources are Borneo, the Philippine Islands and Africa. It is high in tannins, which are extracted for use in tanning, and is a tonnage product.

Divi-divi is the fruit of a tropical American and West Indian tree, *Caesalpinia copiaria*. The fruits are thin pods about 3 inches long, quoted in bags, and used for their tannin content as a tanning and dyeing agent. An extract is also sold.

Valonia, or **valonia cups,** are the dried acorn cups of an oak, *Quercus aegilops*, and of other oaks. They grow in southeastern Europe and Asia Minor. The cups contain 20-40 per cent of tannins, and are often quoted at 32 per cent of tannins. **Valonia beards** are a hairy growth on the acorns of the same tree and are even higher in tannins, being often quoted at 42 per cent of tannins. Both are tonnage products used to supply tannin for the tanning of leather.

Sumac berries or **sumach berries** are obtained from various species of sumac shrubs and trees, *Rhus glabra*. They are imported from Sicily and are also produced in this country. The berries contain tannin, malic and gallic acids, volatile oils and red pigment. Sumac berries are used in the dyeing and tanning industries, and also as an astringent and antidiarrhetic. **Sumac leaves** and **sumac bark** are used to some extent for similar purposes and are quoted as tonnage products. They are high in tannin content and their major use is as a source of raw material for manufacture of sumac extract. **Ground sumac leaves** are quoted.

Nutgalls are excrescences which develop on various species of oak, genus *Quercus*, from the deposit of the eggs of an insect. The U.S.P. standard requires that they be from young twigs. The trees which develop them are native to the Levant. The galls contain 2-4 per cent of gallic acid, 50-60 per cent of tannins, along with resin, gums, etc. Commercial grades are **Aleppo nutgalls** and **Chinese nutgalls.** Medically they are used as an astringent. Industrially they are a source of gallic and gallotannic acids which are important items of trade, and of tanning extracts.

Myrobalans are dried immature fruit obtained from various East Indian trees of the genus *Terminalia*, somewhat resembling prunes in appearance. They contain 20-30 per cent of tannin with resins, fatty acids, etc. Grades sold are J1, J2 and R2. They are used for the production of tanning and dyeing agents. Medically they are used as an astringent and cathartic.

Alkanet root is obtained from several varieties of the genus *Alkanna*, plants growing in Southern Europe and Western Asia. They are high in tannin, and alkanin, a red oil-soluble natural coloring matter. This is soluble in ether, alcohol or benzene. Alkalies convert it to blue. This coloring matter is extracted for coloring, particularly of oils.

Henna or **Egyptian privet,** is the leaf obtained from an Asiatic shrub, *Lawsonia inermis*, which is cultivated along the Mediterranean. The leaves contain coloring matter and tannin and are used mainly as an orange-red coloring agent. This is applied not only to the hair, nails, etc., but also to leather and some textiles. **Powdered henna** consists of the powdered leaves and is also quoted. **White henna** is a variable chemical mixture, unrelated to the botanical henna.

Logwood sticks are small rough logs cut from the heart of the logwood tree, *Hematoxylon campechianum,* growing in the West Indies and Central America. They are imported from Haiti as a tonnage product and are the source of a natural dye obtained by extraction of the wood. There is also some use of logwood as a mild astringent.

Annatto seed is obtained from *Bixa orellana,* a tropical American tree. The pulp of the seed yields a yellowish red dyestuff used for dyeing silk, butter, cheese, oil and wood to yellow or orange colors. Annatto paste is also quoted.

Madder or **Dutch madder** is the pulverized root of *Rubia tinctorum,* a Eurasian plant. It is the natural source of the dye alizarin, now largely displaced by the synthetic material, for use in pigments, dyeing, printing of cotton, etc.

Orris root or **white flag** is the fragrant dried rhizome of several European varieties of *Iris.* It contains iridine, ionone, resin, starch, tannin and 0.1-0.2 per cent of volatile oil. The Florentine or Verona root is sold as fingers or powdered. Medically it is a stimulant and diuretic. Industrially it is used in perfumes, cosmetics, tooth powders, etc. Occasionally individuals are found to be allergic to orris root.

Lavender flowers are the dried flowers, *Lavandula vera,* from the Mediterranean region. Grades are ordinary and selected. They are a nervine, carminative, stimulant and errhine. They are the source of lavender oil, an essential oil used in perfumery. The flowers are also used in cosmetics, and in preparations to repel moths.

Rose flowers are the dried petals of *Rosa gallica* collected just before expanding. This is a U.S.P. X standard. The commercial flowers are sold as red and pale. They are a carminative and astringent. The major use is industrially as a source of rose oil, for distillation to produce rose water, and in cosmetics.

Rosemary flowers and **rosemary leaves** are obtained from the shrub *Rosmarinus officinalis,* which grows in southern Europe and Asia Minor. They are used for the production of oil of rosemary and in perfumery. The flowers are used as emmenagogue, rubefacient, antispasmodic and stimulant.

Orange-flower petals are the dried petals of flowers of the bitter orange *Citrus aurantium* or *Citrus bigardia,* grown in Europe and the United States. They are used for the production of an essential oil, as an odorant in cosmetics, for the preparation of Eau de Cologne and orange-flower water.

Poppy flowers are obtained from the Eurasian poppy plant, *Papaver sommiferum.* The red poppy flowers are used in medicine for making a syrup. **Poppyheads** or **poppy capsules** are the fully grown, dried unripe capsules of the same plant, used as a hypnotic and sedative in place of opium.

Patchouli leaves are obtained from an East Indian shrubby mint, *Pogostemon patchouly,* and are used as a source of patchouli oil.

Pennyroyal consists of the dried leaves and flowering tops of *Mentha pulegium* grown in Europe and Great Britain. It is used as a source of an essential oil and in medicine as a stimulant, carminative and emmenagogue.

Deertongue leaves or **deer's tongue leaves** are obtained from a plant, *Trilisa odoratissima,* which grows in the southeastern part of the United States. It is also known as **wild vanilla.** The leaves contain volatile oils and coumarin. Medically they serve as a tonic and stimulant. Industrially they are used in perfumes and as a flavor in tobacco. A powdered extract prepared *in vacuo* is available.

Hempseed is the fruit of *Cannabis sativa,* an Asiatic herb which is widely cultivated. It is imported from Manchuria for use as food for cage birds and as a source of hempseed oil. **Canary seed** is the seed of canary grass, *Phalaris canariensis.* It is obtained from the Argentine, Morocco and Turkey, and is used as a food for cage birds.

Poppy seed is obtained from the *Papaver sommiferum* or poppy plant. Grades sold are Dutch, Hungarian and Polish. The black seeds are used for coating bakery products and as a source of poppy oil. Quality is usually judged by the presence of broken or crushed seeds and the degree of adventitious contamination. White seeds are sometimes used in pharmaceuticals.

Sunflower seed is the dried ripe seed of *Helianthus annus,* the common sunflower which grows in temperate climates. California sunflower seed includes large and medium grades. The seeds serve as an expectorant and diuretic. An inferior grade is sold for poultry feeding. Industrially they are the source of sunflower oil.

Rapeseed or **napus seed** is obtained from *Brassica napus,* a plant of European origin. The seeds are imported from Belgium, Holland and Japan, and used for the extraction of rapeseed oil.

Pumpkin seed or **pepo** is the dried ripe seed of cultivated varieties of *Cucurbita pepo* grown in Asia, Europe and North America. According to U.S.P. X not more than 5 per cent of broken or defective seed is permitted. Acrid resin, proteins, oil and sugar are present. The seeds are a vermifuge and teniafuge and the source of pumpkin seed oil.

Copra is the dried meat of the coconut, a fruit obtained from the palm *Cocos nucifera,* which grows in the East Indies and South Sea Islands. Copra is a source of a grade of coconut oil, sometimes separately identified as copra oil and used in food products and in soap making.

Millet seed is obtained from the forage grass, millet, *Panicum miliaceum.* It is sold both as whole seed and hulled. Uses are as a cereal grain and as a food for birds.

Soapbark or **quillay** is the dried inner bark of *Quillaja saponaria,* a South American tree. It is sold as pieces, crushed, cut and powdered, largely imported from Chili, and is used industrially as a source of saponin. Soapbark is a stimulant, expectorant, irritant, diuretic and sternutant.

Quassia chips are obtained from the wood of a tropical American tree, *Picrasma excelsa* known in commerce as **Jamaica quassia,** or from *Quassia amare,* known in commerce as **Surinam quassia.** There is a U.S.P. X standard. The chips are also known as **bitterwood** or **bitter ash.** Less common forms are as raspings, shavings or billets. The wood is tough and coarse grained, fibrous, yellowish white to bright yellow with occasional gray pieces. They contain alkaloid, resin, gum, pectin, etc. **Quassia bark** is also sold. Both the chips and bark are used as an anthelmintic, febrifuge, tonic and antiparisitic. Industrially they are used in the preparation of fly paper poisons and hair lotions, as a substitute for hops in brewing, and as a bitter flavoring.

Lycopodium or **vegetable sulfur** is a fine yellow, highly inflammable powder consisting of the spores of *Lycopodium clavatum.* The U.S.P. permits not more than 0.75 per cent of acid-insoluble ash. The plant grows in North America but the product is mainly imported from Europe. The spores contain about 50 per cent of oil. It is used as a cathartic and diuretic. Lycopodium is also a dusting powder and absorbent in excoriations of the skin. Industrially it serves in the manufacture of fireworks.

Fleaseed or **psyllium seed** is obtained from a southern European plant, cultivated in the Far East, *Plantago psyllium.* French or black, and Indian or blond seeds are sold. The small shiny seeds contain a mucilaginous substance and are used in sizing silk, in paper manufacture and in medicine as a laxative.

Quince seed is the seed of *Cydonia vulgaris,* an Asiatic and European tree which is widely cultivated. The seeds contain amygdalin, emulsin, about 15 per cent of fatty glyceride, protein, and about 20 per cent of gum. The gum is extracted from the commercial seed and used medically as a demulcent, and industrially as an emulsifying and thickening agent in cosmetics such as lotions and creams. The dried extract is also available to some extent.

Iceland moss is a dried form of lichen such as *Cetrania islandica,* which grows in mountainous and Arctic regions. It is used as a tonic and demulcent.

Carob seed is derived from *Ceratonia siliqua,* a tree growing near the Mediterranean. The long pods contain, with the seed, a sweet pulp used as a food for animals or man. The seeds were the standard of weight from which the **carat** is derived. The seeds are also known as **carob bean, carob-tree bean, St. John's bread, algarroba** or **algarroba bean** and **locust bean.** From carob seed are derived various extracts sold under trade names, and as **locust-bean gum.** A purified grade, free from starch, has been classed as **locust kernel.** The extract is often classified as **Tragasol,** a trade name. These extracts are only partially water-soluble, and are used as emulsifying agents. Their large-scale use renders them important but standardization is difficult, and products of various producers vary widely in properties. A powdered extract of the seed, prepared *in vacuo,* is available.

Arrowroot is a plant of the genus *Maranta* cultivated in the West Indies, South Carolina, Georgia and many tropical countries. The starch from the roots, **arrowroot starch,** is of a characteristic form, sold as American, St. Vincent and Bermuda grades for uses competitive with other starches. Such uses include as sizing materials, foods, in laundering, etc.

Nux vomica is the dried seed of an Asiatic and Australian tree, *Strychnos nux-vomica.* The U.S.P. standard requires the presence of not less than 1.15 per cent of strychnine. The usual content of mixed nux vomica alkaloids is about 2.5 per cent. The other principal alkaloid is brucine. The seed is sold both whole and powdered. Medically its properties are those of strychnine and brucine of which it is the commercial source.

St. Ignatius' beans, Ignatius beans or **ignatia** are the dried ripe seeds of a Philippine woody vine, *Strychnos Ignatii.* They also grow in Cochin China, and contain about 2 per cent of strychnine and 1 per cent of brucine. The properties and uses are similar to those of nux vomica. A powdered extract, prepared *in vacuo,* is available.

Ipecac consists of the dried rhizomes and roots of varieties of *Cephaelis ipecacuanha,* known in commerce as **Rio ipecac, Brazilian ipecac, Cartagena ipecac, Nicaragua ipecac** or **Panama ipecac.** The plant grows in Brazil and Bolivia and is cultivated in India. The major ingredients of the roots are emetine, cephaeline, psychotrine, ipecacuanhic acid, choline, sugar and resin. The alkaloids of the Cartagena ipecac consist of about 72 per cent of emetine, 26 per cent of cephaeline and 2 per cent of psychotrine. The U.S.P. standard requires not less than 2 per cent of ether-soluble alkaloids of ipecac, and not more than 5 per cent of overground stems or 2 per cent of other foreign organic matter. Ipecac is quoted as root and powder. A dry extract, prepared *in vacuo,* is also sold. Ipecac is used as an emetic, expectorant, vascular sedative, diaphoretic and antidysenteric. It is the source of emetine, and a **deemetinized ipecac** is sold.

Cocillana bark, cociliana bark or **cocilliana bark** is the dried bark of various *Guarea* growing in Bolivia. It contains resins, fat and tannins and resembles ipecac in properties. It is a cathartic.

Cinchona bark or **Peruvian bark** is the dried bark of various species of *Cinchona,* known in commerce as **red cinchona** or **yellow cinchona.** Cinchona grows in South America and is raised in India. The latter is the main commercial source. It contains at least 35 different alkaloids but the content is largely quinine. The U.S.P. standard requires that at least 5 per cent of alkaloids be present. Various grades sold include quils, long, broken and chips, as well as high-test bark and chips of bark. It is the source of quinine and other cinchona alkaloids, and is a febrifuge, antiperiodic, astringent and tonic. A grade comes from Ecuador as **pale cinchona** in tubes. A powdered extract of the red variety, prepared *in vacuo,* is available.

Aconite, monkshood or **wolfsbane,** is a poisonous plant, *Aconitum napellus,* from which both leaves and root are recovered. Only the dried tuberous roots are U.S.P. They may contain not more than 5 per cent of stems nor more than 2 per cent of other foreign organic matter. The leaves are permitted by the British Pharmacopoeia. A powdered extract of the root, prepared *in vacuo,* is sold. The plant grows in the mountainous areas of Asia, Europe and North America. The roots contain about 0.4 per cent of aconitine along with other alkaloids. It is a diaphoretic, antipyretic, myotic, anodyne and sedative, and a source of alkaloids.

Digitalis or **fox glove** consists of the dried leaves of the purple foxglove, *Digitalis purpurea.* The U.S.P. standard permits not more than 8 per cent of moisture, not more than 2 per cent of stems, browned leaves, flowers or foreign organic matter, and not more than 5 per cent of acid-insoluble ash. The potency also must be such that 0.1 gram has an activity of 1 U.S.P. digitalis unit. This is identical with the International unit. It is used in powdered form. Digitalis grows in Europe and the United States and contains 0.2-0.4 per cent of digitoxin with other alkaloids, resins, etc. It is used as a sedative, narcotic, aphrodisiac, heart tonic, vascular stimulant and diuretic. A powdered extract, prepared *in vacuo,* is available.

Belladonna leaves and **belladonna root** are both U.S.P. products. The leaves are the dried leaves and tops of *Atropa belladonna* or **deadly nightshade,** and contain not more than 3 per cent of stems over 10 mm. in diameter and yield not over 3 per cent of acid-insoluble ash. Over 0.3 per cent of alkaloids must be present. The U.S.P. root of the same shrub contains not more than 10 per cent of stem bases and woody crowns, not more than 2 per cent of other foreign organic matter and gives not more than 4 per cent of acid-insoluble ash. Not less than 0.45 per cent of alkaloids is present. The plant grows in Europe, Asia Minor and northern Africa and is raised in the United States. Both leaves and root are quoted and contain atropine, hyoscyamine and scopalamine with organic acids. They are used as sources of the alkaloids and as a sedative, antispasmodic, mydriatic, anodyne and narcotic. Dried extracts, prepared *in vacuo* from both leaves and root, are available.

Conium, hemlock, poison parsley or **spotted cowbane** is usually the leaves of a poisonous herb, *Conium maculatum,* growing in Asia, Europe and the United States. The unripe, carefully dried fruit is also used. They contain the liquid alkaloid, coniine, with related alkaloids, volatile oil, etc. Either form is used as antispasmodic, aphrodisiac, anodyne, soporific, narcotic and sedative. The leaves and fruits are also the commercial source of coniine. A dried extract from the leaves, prepared *in vacuo,* is available.

Strophanthus seeds are the dried, ripe seeds of *Strophanthus kombe,* and a related species of tropical African and Asiatic tree or shrub, the seed being deprived of the awns. They contain 8-10 per cent of the glucoside strophanthin, along with trigonelline, fixed oil, etc. There is a U.S.P. X standard based on the strength of a tincture measured by injection into a frog. A dry extract, prepared *in vacuo,* is available. The seeds are medically a stimulant and diuretic, much like digitalis. Industrially they are the source of strophanthin of U.S.P. standard.

Stramonium or **thorn apple** consists of the dried leaves and flowering tops of the **jimson weed,** *Datura stramonium.* Supplies are largely imported from Europe. The U.S.P. standard requires the presence of not less than 0.3 per cent of alkaloids and not more than 3 per cent of stems over 8 mm. in diameter. The acid-insoluble ash must not exceed 4 per cent. A powdered extract, prepared *in vacuo,* is sold. The leaves contain the alkaloids atropine, hyoscyamine and scopolamine along with albumins, gums, etc. They are used as a diuretic, antispasmodic, narcotic, nervine, mydriatic and hypnotic. They are smoked to relieve asthma. In both composition and use they are similar to belladonna. **Stramonium seed** is also sold.

Calabar beans are the dried ripe seeds of *Physostigma venenosum,* a tropical woody vine. They contain physostigmine and in U.S.P. X were required to have a 0.15 per cent alkaloid content. They grow in West Africa, India and Brazil. The beans are used in medicine as a motor depressant, sialagogue, sedative, diuretic, myotic, antineuralgic, diaphoretic, purgative, antitetanic, antispasmodic and tonic. They are the commercial source of physostigmine.

Wormseed is not a true seed. **American wormseeds** are the unexpanded flowerheads of a native plant of the genus *Artemesia.* **Levant wormseed** consists of similar flowerheads of *Artemesia maritima* or *Artemesia pauciflora* grown in Persia, Turkestan and Russia. The American material is of low quality. Levant wormseed contains 2-5 per cent of santonin. The product is used as an anthelmintic and as the source of santonin.

Barberry root bark is the bark of the rhizome of *Berberis vulgaris.* It is a laxative, febrifuge, astringent and bitter tonic and is also a source of berberine and of a yellow dye. **Barberry bark** is also quoted at a somewhat lower price.

Jaborandi or **pilocarpus** consists of the dried leaflets of *Pilocarpus jaborandi,* a South American shrub. They contain about 0.5 per cent of pilocarpine along with other alkaloids. A powdered extract of the leaves, prepared *in vacuo,* is available. The uses are similar to those of pilocarpine and the leaves are the commercial source of that alkaloid. **Colchium seed** is the dried ripe seed of *Colchium autumnale* obtained from a European and northern African herb of the bunch-flower family. The U.S.P. standard requires 0.45 per cent of colchicine. It contains 6-8 per cent of oil with the usual tannins, starches, gums, etc. A powdered extract, prepared *in vacuo,* is available. The seed is used in medicine for its emetic, sedative, diuretic and cathartic action, and for the extraction of the alkaloid, colchicine.

Ergot is the dried sclerotium of *Claviceps purpurea,* a fungus growth which develops on rye plants. It contains several alkaloids such as ergotoxine, ergotamine and ergotinine. The U.S.P. standard requires that each gram be equivalent by biological assay to not less than 0.5 mg. of ergotoxine ethanesulfonate. Not more than 8 per cent of moisture nor more than 4 per cent of seeds, fruit and foreign organic matter are permitted. The product is cultivated and imported from Russia, Poland and Spain, and quoted by the U.S.P. standard. It is used in medicine as a parturient, emmenagogue, excitomotor, hemostat and echolic. A dry extract, prepared *in vacuo,* is also available.

Cannabis or **Indian hemp** consists of the dried flowering tops of the pistillate plants of an herb, *Cannabis sativa,* from which the resin has not been removed. The U.S.P. standard requires not more than 10 per cent of fruits, large foliage leaves, and stems over 3 mm. in diameter, not more than 2 per cent of other foreign organic matter, and not more than 5 per cent of acid-insoluble ash. The plant is grown in Persia, India, Europe and the United States and contains an alkaloid. Uses are as an anodyne, nervine, sudorific, aphrodisiac, hypnotic and diuretic. It is used by some drug addicts for smoking in cigarettes, and therefore controlled by the same type of laws as cover other habit-forming drugs.

Henbane, or **hyoscyamus** is the dried leaf with or without the tops, of *Hyoscyamus niger,* which grows in Europe, Asia and the United States. The U.S.P. standard permits not more than 25 per cent of stems no more than 7 mm. in thickness, not more than 12 per cent of acid-insoluble ash, and not less than 0.04 per cent of alkaloids. In U.S.P. X the requirement was 0.065 per cent of alkaloids. A powdered extract, prepared *in vacuo,* is available. The seeds may be used, but are not official. Among the alkaloids are hyoscine or scopalamine, and hyoscyanine, along with choline, mucilage, etc., which are much higher in the seeds than in the plant. Uses are as an anodyne, hypnotic, mydriatic, narcotic, antispasmodic and laxative.

Serpentaria, snakeroot or **birthwort** consists of the dried rhizomes and roots of varieties of *Aristolochia serpentaria,* known in commerce as **Virginia snakeroot** or **Texas snakeroot.** The U.S.P. standard does not permit over 10 per cent of the overground stems nor more than 2 per cent of other foreign organic matter, and not more than 10 per cent of acid-insoluble ash. Serpentaria contains about 1 per cent of volatile oil with resin and tannin. Uses are as aphrodisiac, stimulant, antiperiodic, expectorant, tonic, diaphoretic, diuretic and emmenagogue.

Gentian or **bitter root** consists of the dried rhizomes and roots of the yellow gentian, *Gentiana lutea.* It is U.S.P. and contains not less than 30 per cent of water-soluble extractive, not more than 10 per cent of moisture and not more than 2 per cent of foreign organic matter. The U.S.P. standard covers both the unground and powdered grades. It is also sold as a ground rather than as a powdered grade. A powdered extract, prepared *in vacuo,* is available. Aside from use in the manufacture of liquors it is a pharmaceutical excipient, tonic and laxative.

Rhubarb or **rheum** consists of the dried rhizomes and roots of *Rheum officinale,* which grows in China and Tibet. It is cultivated in Europe and Siberia. The U.S.P. product requires not less than 30 per cent of dilute alcohol-soluble extractive. The powdered product is used in medicine as a cathartic, astringent, stomachic and tonic. A dry U.S.P. extract, prepared *in vacuo,* is available.

Valerian root consists of the dried rhizomes and roots of *Valeriana officinalis.* It grows in Europe, northern Asia and eastern United States. The U.S.P. product requires not more than 5 per cent of foreign organic matter and not more than

10 per cent of acid-insoluble ash. A powdered extract, prepared *in vacuo,* is also available. Valerian root acts as an antispasmodic, anodyne, nervine and stimulant.

Althea root or **marshmallow root** is the dried root of the marshmallow, *Althea officinalis,* deprived of the rootlets and of the brown, corky layer. It must not contain more than 1 per cent of foreign organic matter according to the U.S.P. standard. It grows in Europe, northwest Asia and the eastern United States, and contains asparagin, about 30 per cent of mucilaginous materials, starch, pectin and sugar. Commercially it is offered cut in cubes. It is used medically as a demulcent and emollient. **Althea leaves** or **marshmallow leaves** are also sometimes so used but are not U.S.P.

Mandrake root or **may apple** consists of the dried rhizomes of *Podophyllum peltatum.* It is a U.S.P. product containing not less than 4 per cent of podophyllum resin and not more than 3 per cent of foreign organic matter. Both unground and ground forms are specified. The plant grows in North America. It is used as a tonic, purgative, alterative, hydragogue and cholagogue. A dry extract, prepared *in vacuo,* is also available. **Indian mandrake** is a British Pharmacopoeia product used as a purgative.

Jalap root is the dried tuberous root of *Exogonium jalapa* from a plant growing in Mexico and cultivated in India. Supplies are largely from Mexico. U.S.P. X requires not less than 7 per cent of resins. B.P. requires not less than 9 nor more than 11 per cent of resins. The root contains up to 20 per cent of resins, with starch and sugar. It is quoted as a powder and in NF grades, for use as a strong purgative, diuretic and anthelmintic. A powdered extract, prepared *in vacuo,* is also available.

Colocynth pulp is the dried pulp of the unripe but fully grown fruit of a Mediterranean vine, *Citrullus colocynthis,* also known as **bitter apple.** U.S.P. X permits not more than 5 per cent of seed nor 2 per cent of epicarp. Not more than 2 per cent should be soluble in purified petroleum benzene and not more than 6 per cent of acid-insoluble ash is permitted. It is used as a purgative, emmenogogue and diuretic. A dry extract, prepared *in vacuo*, is also sold.

Senna consists of the dried leaflets of *Cassia augustifolia,* which grows in eastern Africa and western Asia. The U.S.P. requires that it contain not more than 8 per cent of stems, nor more than 2 per cent of pods or other foreign organic matter. The acid-insoluble ash must not exceed 3 per cent. The Alexandria and Tinnevelly grades are quoted as numbers 1, 2, 3, powdered and siftings. **Senna pods** are also sold. The various forms are used as a purgative. Dried extracts, prepared *in vacuo* of both leaves and pods are available.

Goldenseal root consists of the dried rhizomes and adventitious roots of *Hydrastis canadensis*, a North American shrub cultivated on a large scale. It was required by U.S.P. X to contain not less than 2.5 per cent of ether-soluble alkaloids. Goldenseal root contains 1.5-3.2 per cent of hydrastine, about 3 per cent of berberine, together with canadine, volatile oil and resins. Beside the U.S.P. root, a powdered extract, a solid extract and a concentrate, prepared *in vacuo,* are available. Goldenseal is used as an alterative, antihydrotic, bitter tonic, hymostatic in uterine hemorrhages, antiperiodic, cholagogue and astringent, and as a source of hydrastine and berberine. It is sometimes called **hydrastis root,** also **yellowroot**; the latter is correctly the root of *Zanthorrhiza opiifolia,* also a North American shrub.

Scammony root is the dried root of *Convolvulus Scammonia,* a vine native to Asia Minor. It is used in medicine as a strong cathartic, hydragogue and cholagogue. The vine grows in Greece, Asia Minor and Northern Africa. In U.S.P. IX it was required to contain 8 per cent of resin.

Cascara sagrada bark is the dried bark of *Rhamnus purschiana,* a California buckthorn. The U.S.P. standard requires not more than 4 per cent of foreign organic matter, and that it be aged one year after collection, to reduce the griping action. It grows in the northwestern United States and contains emodin, frangulin, oils, resins and tannins. Cascara is used as a cathartic and rheumatic. A dried extract, prepared *in vacuo*, is available in powdered form, granular, as a bitter solid, a bitter-less solid, and an aromatic solid. **Cascara sagrada berries** are similarly used but are not U.S.P.

Elm bark is the dried inner bark of *Ulmus fulva*, the **slippery elm** tree which grows in North America. It contains largely gums, with little tannin. It was a U.S.P. X product. Grades sold are grinding, powdered and select bundles. It is used in medicine as a demulcent and nutrient.

Buchu leaves are obtained from a South African plant, several varieties of *Barosma* being used. According to U.S.P. X this must not contain more than 8 per cent of stems nor more than 2 per cent of other foreign organic matter. They contain 1.3-2 per cent of volatile oil along with barosma camphor, resins, etc., and are a stimulant, tonic, diaphoretic and diuretic. A dried extract, prepared *in vacuo*, is available.

Eucalyptus leaves are the dried scythe-shaped leaves of *Eucalyptus globulus*, a tree which grows in Australia and subtropical countries. According to U.S.P. X not more than 3 per cent of stems, fruits or other foreign organic matter are permitted. About 1-3 per cent of volatile oil is present with tannins, resins, etc. The leaves are used as an astringent, expectorant, antipyretic, antiseptic, antispasmodic, febrifuge, stimulant, tonic and hemostatic. The fresh leaves are distilled to produce oil of eucalyptus, which is a U.S.P. product.

Lobelia or **Indian tobacco** consists of the dried leaves and tops of a North American plant, *Lobelia inflata*. According to U.S.P. X they contain not more than 10 per cent of stems nor more than 2 per cent of other foreign organic matter, and yield not more than 5 per cent of acid-insoluble ash. A dried extract, prepared *in vacuo*, is also available. Lobelia is a narcotic, purgative, diuretic, diaphoretic, expectorant, nervine, emetic and antispasmodic. **Lobelia seed** is sold for similar use.

Uva ursi leaves or **bearberry leaves** are obtained from a plant, *Arctostaphylos uva ursi*, which grows in the north temperate zone. U.S.P. X permits not more than 5 per cent of stems or other foreign organic matter. The leaves contain bitter glucosides, arbutin, quercitin, organic acids, etc., along with resins and 6-7 per cent of tannin. They serve as emmenagogue, emetic, cathartic, antilithic, diuretic, nephritic and tonic.

Prince's pine herb or **ground holly** consists of the dried leaves of *Chimaphila umbellata,* which grows throughout the northern hemisphere, and is a diuretic, tonic, astringent, nephritic and rubefacient. It is similar in many ways to Uva ursi.

Yerba santa leaves are the dried leaves of *Eriodictyon californicum.* The U.S.P. standard requires not more than 5 per cent of stems nor more than 2 per cent of other foreign organic matter. A solid extract, prepared *in vacuo,* is also available. The leaves come from California and are used as expectorant, tonic, stimulant, anticatarrhal and alterative.

Pellitory root or **pyrethrum root** is obtained from *Anacyclus pyrethrum,* native to North Africa. It contains about 50 per cent of inulin, together with volatile oil and pyrethrins. The root is used in medicine as a sialagogue and masticatory in headache, toothache and neuralgic affections of the face.

Berberis root or **barberry root** is obtained from the shrub of the genus *Mahonia,* which grows in the United States and Canada. It contains berberin, oxycanthine and berbamine and is used in medicine as a tonic, antiperiodic, febrifuge, alterative and diuretic. A powdered extract, prepared *in vacuo,* is available.

Beth root or **trillium root** is the dried root of various species of *Trillium erectum,* growing in Canada, the United States and Japan. It is used as an astringent, tonic, alterative and expectorant.

Black Indian hemp root, Canadian hemproot, or **apocynum root** is obtained from a plant, *Apocynum cannabinum,* which grows in North America. It is used as a diuretic, sudorific, diaphoretic, alterative, antiperiodic, expectorant and tonic, in some cases following administration of digitalis. A solid extract, prepared *in vacuo,* is available.

Bloodroot or **Sanguinaria** consists of the dried roots and rhizomes of a plant, *Sanguinaria canadensis,* which grows in North America. The ground root is used as an expectorant, stimulant, emetic, sternative, emmenagogue and tonic. A solid extract, prepared *in vacuo,* is available.

Blueflag root, flag lily, iris, or **water flag** is the dried rhizome of varieties of *Iris versicolor,* growing in North America. It is used as a cathartic, diuretic, emetic, alterative and cholagogue. A powdered extract, prepared *in vacuo,* is available.

Bryonia is the dried root of various varieties of *Bryonia alba.* Alkaloid and resin are present. Medically it is a vesicant, emetic, emmenagogue and purgative.

Burdock or **lappa** is the dried first-year root of the common burdock, *Arctium lappa,* growing in Europe, Asia and North America. It contains inulin, tannin and volatile oil and is used as an alterative, diuretic, aperient, diaphoretic and cathartic. Burdock is applied externally to swellings and burns. A powdered extract, prepared *in vacuo,* is available. **Burdock seed** and **burdock herb** are also used similarly.

Cohosh, cimicifuga, bugroot or **black snake root** consists of the rhizomes and roots obtained from several North American plants and is sold as black from *Cimifuga racemosa,* and blue from *Caulophyllum thalictroides.* It is used in medicine as an emmenagogue, expectorant, diaphoretic, antispasmodic, diuretic and sedative.

Columbo root, calumba root or **colombo root,** is obtained from an East African plant, *Jateorrhiza salmata,* and is used in medicine as a tonic, stomachic, astringent, stimulant and anthelmintic. A powdered extract, prepared *in vacuo,* is available.

Cranesbill or **geranium** is the dried rhizome of *Geranium maculatum,* grown in Canada and the eastern United States. It is high in tannin and serves as a styptic and astringent.

Dandelion or **taraxacum** consists of the dried rhizomes and roots of the common dandelion of Europe and America, *Leontodon taraxacum.* It is used in medicine as a diuretic, stomachic hepatic stimulant and tonic. The German roots are quoted. A dry extract prepared *in vacuo* is available.

Culver's root, black root or **Leptandra** consists of the dried rhizomes and roots of *Leptandra virginica,* common in North America. It is used in medicine as a cathartic, emetic, alterative, tonic and cholagogue. A dried extract and a concentrate, both prepared *in vacuo,* are available.

Doggrass root or **triticum** consists of the dried rhizomes and roots of *Agropyron repens,* gathered in the spring. It grows in Europe, northern Asia and the United States and is used as an aperient and diuretic. A dried extract, prepared *in vacuo,* is available.

Echinacea root consists of the dried rhizomes and roots of a North American herb, *Brauneria pallida* or *Brauneria augustifolia,* members of the thistle family. It is used externally for the treatment of boils and ulcers, and contains an acrid resin. Its action is as a febrifuge, antiseptic, analgesic, alterative and aphrodisiac. A powdered extract, prepared *in vacuo,* is available.

Elecampane, inula or **scabroot,** consists of the dried rhizomes and roots of an herb, *Inula helenium,* grown in the United States, Europe and Central Asia. It is used in medicine as a tonic, stimulant, expectorant, diaphoretic, diuretic and emmenagogue.

Galangal root, colic root, or **Chinese ginger** consists of the dried rhizomes of a Chinese plant, *Alpinia officinarum,* and is used in medicine as an aromatic, stimulant and stomachic.

Gelsemium or **wild woodbine** is the dried rhizomes and roots of the yellow jasmine, *Gelsemium sempervirens,* grown in the southern United States. It is used as a sedative, mydriatic, antispasmodic, diaphoretic, antineuralgic and antiperiodic. A solid extract, prepared *in vacuo,* is available.

Ginseng or **panax** is the aromatic root of *Panax quinquefolium,* a North American herb, or *Panax schinseng,* a Chinese herb. It is used mostly by the Chinese as a panacea for many diseases and is a stimulant, aphrodisiac, nervine and tonic.

Hydrangea root consists of the dried rhizomes and roots of the *Hydrangea arborescens* grown in the eastern United States. It contains saponins, with oils, starches and resins, and is used as a diuretic and antilithic. A powdered extract, prepared *in vacuo,* is available.

Kava, kava kava, ava-ava or **kawa** consists of the dried rhizomes and roots of *Piper methysticum,* a Polynesian shrub. It contains an alkaloid, kavaine, and is used as a diuretic, genitourinary, antiseptic, sialagogue, sudorific, tonic, stimulant and anticatarrhal, and as a source of kava kava oleoresin. A dry extract of the root, prepared *in vacuo,* is available.

Lovage root or **sea parsley root** is from *Levisticum officinale*, grown in southern Europe and the United States. Both domestic and imported grades are sold. It is used in medicine as an aromatic stimulant, in amenorrhea and as a diuretic. A solid extract, prepared *in vacuo*, is available.

Lady slipper or **American valerian** consists of the dried rhizomes and roots of *Cypripedia* found in central and eastern North America. It is used as an antispasmodic, stimulant, nervine and analgesic.

Manaca root, vegetable mercury or **manacan** is the dried root of *Brunfelsia hopeana*, which grows in Brazil and the West Indies. It contains an alkaloid, **manacine.** Medically it is a diuretic, cathartic, antisyphilitic, antiscrofular, alterative and antirheumatic. A solid extract, prepared *in vacuo*, is available.

Musk root, or **sumbul** consists of the dried rhizomes and roots of *Ferula sumbul*, found in central Asia and the East Indies. It is used as a carminative, nervine, stimulant, antispasmodic and tonic. A solid extract, prepared *in vacuo*, is available.

Pareira or **pareira brava root** is the dried root of *Chondrodendron tomentosum*, a variety of South American vine. It contains about 10 per cent of pelosine, and is used in medicine as a diuretic, emmenagogue, aperient and febrifuge. A powdered extract, prepared *in vacuo*, is available.

Pinkroot or **spigelia** consists of the dried rhizomes and roots of *Spigelia marilandica*, which grows in eastern North America. It contains the alkaloid **spigeline,** and is used in medicine as an anthelmintic, mydriatic and narcotic.

Pleurisy root or **asclepias** is the dried root of the **butterfly weed,** *Asclepias tuberosa*. It grows in the northern United States and southern Canada. The root is used as a diaphoretic, cathartic and expectorant.

Poke root is the dried root of *Phytolacca americana*, growing in temperate climates of North America and Europe. It is used as an alterative, emetic, purgative and cathartic. A solid extract and a concentrate, both prepared *in vacuo*, are available.

Rhatany root or **Krameria** is the dried root of the Peru rhatany, *Krameria triandra*, or Brazilian rhatany, *Krameria argen-*

tea. It was a U.S.P. product. The tannic acid content is over 8 per cent and it possesses astringent properties similar to those of tannic acid. It is used as an astringent and tonic. A solid extract, prepared *in vacuo,* is available.

Senega root or **Seneca snakeroot** is the dried root of *Polygala senega.* It grows in eastern North America and contains an irritating saponin. Senega root is used in medicine as an expectorant, diuretic, alterative, sedative and diaphoretic. A powdered extract, prepared *in vacuo,* is available.

Asarum, Canada snakeroot or **wild ginger** consists of the dried rhizomes and roots of *Asarum canadense,* a plant grown in Canada, North Carolina and Kansas. It contains acrid resin, aromatic volatile oil, methyl eugenol, gum, chlorophyll, etc. It is used in medicine as an aromatic, stimulant and diaphoretic.

Skunk cabbage root is the dried root of an herb, *Symplocarpus foetidus,* which grows in North America and Asia. It is used in medicine as a stimulant, antispasmodic and narcotic.

Stillingia or **queens root** is the dried root from *Stillingia sylvatica* of the southeastern United States. It may contain an alkaloid, **stillingine,** along with acid resin, fixed oil, starch, glucosides, tannin, gum and 3-4 per cent of volatile oil. Uses are as sialagogue, diaphoretic, cholagogue, diuretic, alterative, antisyphilitic, expectorant, antiscrofular and emetic. A powdered extract, prepared *in vacuo,* is available.

Spikenard or **aralia** consists of the dried rhizomes and roots of *Aralia racemosa,* grown in the eastern United States. It is used as a diaphoretic, alterative and stimulant.

Stoneroot or **collinsonia** is the root of *Collinsonia canadensis* growing in eastern North America. It is used in medicine as a tonic, diuretic, diaphoretic, antispasmodic, astringent and anticatarrhal agent.

Unicorn root, colic root or Aletris is the dried rhizomes and roots of *Aletris farinosa.* It grows in the eastern United States and consists principally of starch and a bitter principle. It is used as a tonic, diuretic, laxative, emetic and vermifuge. This is referred to as true unicorn root and **helonias** from *Chamaelirium luteum,* as **false unicorn root.** The latter is used for the same purposes. Curiously enough the false is twice as expensive as the true. A powdered extract of helonius root, prepared *in vacuo*, is available.

Wild indigo, false indigo or **baptisia** is the root of *Baptisia tinctoria*, native to North America. The roots contain an alkaloid and at least two glucosides. It is used as an antiseptic, astringent and cathartic. A powdered extract, prepared *in vacuo*, is available.

Yellow dock or **rumex** is the dried root of *Rumex crispus*, native to the United States and Europe. The root contains emodin and tannins and is used in medicine for its astringent, tonic. laxative and alterative properties. A solid extract, prepared *in vacuo* is available.

Dogwood bark is the bark of the root of the **white dogwood,** *Piscidia Erythrina*, growing in the West Indies as *Ichthyomethia Piscipula* and in Florida as *Piscidia erythrina*. Domestic and Jamaica grades are quoted. The bark contains a glucoside and is used in medicine as alterative, sedative, anodyne, diuretic, hypnotic and narcotic. It is one of the fish poisons, containing **piscidin** instead of rotenone.

Angostura bark is the bark of *Cusparia trifoliata* and related species of trees which grow in the northern part of South America and the West Indies. The bark contains about one per cent of ethereal oil, a glucoside, resin, etc. It is used in medicine as a stimulant, tonic, febrifuge, emetic and cathartic.

Black-haw root bark is obtained from *Viburnum prunifolium*, the virburnum shrub. **Black-haw tree bark** and **black-haw roots** are also sold. They grow in the United States and contain various tannins and resins. They are used as a nervine, tonic and sedative. A powdered extract, prepared *in vacuo*, is sold.

Frangula, black dogwood or **buckthorn bark** is from *Rhamnus frangula*, a thorny shrub which grows in Europe, western Asia and northern Africa. The British Pharmacopoeia requires that it be matured at least one year. Among other things it contains emodin, resins and tannins. It is a tonic, cathartic and diuretic. A solid extract, prepared *in vacuo*, is available. **Buckthorn berries** are the dried ripe berries of *Rhamnus cathartica* and contain similar principles in a much more concentrated form.

Butternut bark is the dried inner bark of the root of the butternut tree, *Juglans cinerea,* and is collected in the autumn. It grows in North America and contains resins, juglone, tannins and fixed volatile oils. Uses are as an antiperiodic, alterative, hepatic and a mild cathartic.

Condurango bark is the dried bark of *Marsdenia condurango,* a vine growing in Ecuador and Peru. It contains a poisonous glucoside and a trace of alkaloid. It is used for the relief of various types of ulcer. A dried extract, prepared *in vacuo,* is available.

Cramp bark is the dried bark of *Viburnum opulus,* the high bush **cranberry.** Grades sold are "genuine" and "so-called" cramp bark, the latter at a much lower price, from *Acer spicatum.* The barks contain oxalates, citrates and malates as well as tannin, sugar and resin, and are used as a tonic, diuretic, astringent, antispasmodic and nervine. Solid extracts of both barks, prepared *in vacuo,* are available.

Cottonroot bark or **gossipium bark** is the dried root bark of cultivated varieties of *Gossypium herbaceum,* or cotton. Cotton is grown in many parts of the world. The bark contains yellow color, resin, fixed oil and sugar. It is an emmenagogue and oxytocic. A solid extract, prepared *in vacuo,* is available.

Fringetree bark is the dried root bark of *Chionanthus virginica,* a tree which grows in the southern part of the United States. It contains a glucoside and traces of saponins and is used as laxative and diuretic. A solid extract and a concentrate, both prepared *in vacuo,* are available.

Pomegranate bark is obtained from the stem of a plant, *Punica granatum,* growing in semitropical countries. It contains 0.5-1 per cent of alkaloids and is used as an astringent, teniafuge and anthelmintic.

Prickly ash bark is the dried bark of varieties of *Xanthoxylum americanum,* or **angelica tree.** It grows in North America and contains **xanthoxylin,** which is probably an alkaloid. It is used in medicine as a counter-irritant, stimulant, alterative and emmenagogue, and as a source of the active principle xanthoxylin. A dried extract, prepared *in vacuo,* is available. **Prickly ash berries** are also sold for similar use.

Simaruba bark is obtained from a tropical American tree, *Simaruba amar,* and is used in medicine as a bitter tonic and astringent.

Tonga vine is a mixture of about equal parts of the bark of *Premna arborea* and the root of *Epipremnum pinnatum.* It comes from Malasia and Australia and contains an alkaloid **tongine.** It is used as an analgesic in neuralgia. The NF grade is quoted.

Wahoo-root bark is obtained from various shrubs of the genus *Euonymus atropurpureus,* growing in the eastern part of the United States. Among the ingredients are a resinoid, euonymin, organic acids, etc. It is used in medicine as a tonic, cathartic, diuretic, expectorant, cholagogue, antiperiodic and antiparasitic. A solid concentrate, prepared *in vacuo,* is available. **Wahoo-tree bark** is similarly used and is less expensive but lower in active materials.

White-pine bark is the inner bark of the white pine, *Pinus strobus,* growing in the eastern part of North America. It is sold as a grade having the rough outer bark removed, called **rossed,** and is used in making cough sirups. A dried extract, prepared *in vacuo,* is available.

Catnip, catnep or **catmint** is an herb, the common, strongly scented catnip shrub, *Nepeta cataria.* It grows in Asia, Europe and the United States and contains volatile oil and tannin. It is used as a sedative, emmenagogue and carminative. A solid extract, prepared *in vacuo,* is available.

Coltsfoot or **coughwort** consists of the dried leaves of *Tussilago farfara,* growing in the United States, Europe and Asia. The dried flowers are also used. The leaves contain saponin, wax and rubber with pectin, glucosides and tannins. The flowers contain the last three. It is a demulcent, tonic, errhine and emollient. A solid extract, prepared *in vacuo* from the leaves is available.

Damiana leaves are the dried leaves of two varieties of *Turnera,* which grow in tropical America, California and Texas. They are used in medicine as a stimulant, tonic, aphrodisiac and diuretic. A powdered extract, prepared *in vacuo,* is available.

Liverwort leaves consist of the entire *Hepatica* plant, which grows in Europe. The product is used as an astringent and tonic, containing mainly tannins and oleoresin.

Matico leaves consist of the dried leaves of *Piper angustifolium,* which grows in South America, Mexico and Cuba. They contain 1-3.5 per cent of volatile oil, with tannins, gums, etc. The leaves are used in medicine as an aromatic, stimulant, alterative, hemostatic, anticatarrhal, astringent and tonic.

Mullein flowers are the dried corollas with adhering stamens obtained from varieties of *Verbascum thapsis,* growing in Europe and Asia. The action is as diuretic, anodyne, antispasmodic, demulcent, diaphoretic and antiperiodic. **Mullein leaves** are similarly derived and used. A solid extract of the leaves, prepared *in vacuo,* is available.

Pichi leaves are obtained from *Fabiana imbricata,* growing in Chile and Peru. The branches and wood are similar. They are used as anticatarrhal, cholagogue and diuretic. A powdered extract, prepared *in vacuo,* is available.

Queen of the meadow, trumpet weed or **purple boneset** consists of the dried leaves and flowering tops of a native plant *Eupatorium purpureum.* The product is used in medicine as a bitter tonic, diaphoretic, and feeble emetic. **Queen-of-the-meadow root,** *Filipendula ulmaria,* is similarly used. A dried extract of the root, prepared *in vacuo,* is available.

Squaw vine or **checkerberry** consists of the dried vine or the dried leaves of the North American or Japanese *Mitchella repens.* The product is used as diuretic, astringent and tonic. A dried extract, prepared *in vacuo,* is available.

St. John's wort is a dark brown mixture of dried leaves and twigs obtained from a plant of the genus *Hypericum.* It grows in Europe, Asia and the United States. The main ingredients are tannins, pigment and volatile oil. It is used as a stimulant and diuretic.

Tansy leaves or **tanzy leaves** are the dried leaves and tops of *Tanacetum vulgare* growing in Europe, Asia and North America. They contain organic acids, resin, tannin, gum, etc. The leaves are used as an emmenagogue, anthelmintic, tonic, stimulant, diuretic, diaphoretic and abortifacient.

Cumin seed is obtained from the dwarf plant, *Cuminum cyminum,* native to Egypt, Syria and nearby countries. Some 3-4 per cent of volatile oils are present. Cumin seed is imported from Algeria, Morocco and India. The aromatic seed is used in flavoring materials, and as a stimulant and carminative.

Gold-of-pleasure seeds are the dried seeds of *Camelina sativa,* an herb growing naturally in Europe and naturalized in North America. They are used medicinally.

Guarana or **Brazilian cocoa** is a dried powder consisting of the crushed seeds of a Brazilian climbing shrub, *Paulinia cupana.* The powder contains 2.5-5 per cent of caffeine and is used in medicine as an astringent, stimulant, tonic, nervine and antineuralgic. **Guarana paste** is also sometimes sold.

Larkspur seed is the dried ripe seed of *Delphinium ajacis,* which grows in Central Europe and the United States. It is a diuretic, anthelmintic, emmenagogue and aperient.

Cubeb berries or **Java pepper berries** are the dried unripe, but nearly fully grown, fruit of a Javanese shrub, *Piper cubeba,* cultivated in the West Indies and Ceylon. The berries contain 10-20 per cent of volatile oils, with resin, fat, etc., and about 20 per cent of oleoresin. The whole and ground berries are sold. The latter are used in the treatment of catarrh and as an aromatic stimulant, local irritant, diuretic, carminative and sedative. A solid extract, prepared *in vacuo,* is available.

Laurel berries or **bay berries** are the ripe fruit of a shrub, *Laurus nobilis,* grown in Mexico and along the Mediterranean. They contain some 30 per cent of oil, largely nonvolatile. The source is largely Italian. Medically they are a stomachic. Industrially they are the source of an oil used as an odorant, but this is not the bayberry oil or oil of bay of commerce, which is from other sources. **Laurel leaves** from the same sources are also sold and are used similarly.

Ephedra is usually the leaves and branches of *Ma huang* or *Ephedra vulgaris,* grown in Japan, China and India. *Ephedra nevadensis* is of the same genus. The product is the source of ephedrine, an alkaloid, and also serves as an astringent. A solid extract, prepared *in vacuo,* is available.

Kola nuts or **Soudan coffee** are the dried seeds of various varieties of *Cola,* growing in Africa, India and other tropical areas. They contain 2-2.5 per cent of caffeine with theobromine, glucosides, gum, starch, etc. They are used as an astringent, aphrodisiac, diuretic, nervine, tonic and stimulant. A solid extract, prepared *in vacuo*, is available.

Coco leaves are the dried leaves of various varieties of *Erythroxylon*, particularly those known commercially as **Huanaco coco** and **Truxillo coco.** They grow in various countries on the west coast of South America, and in Java. The leaves contain substantial amounts of alkaloids, often one per cent of cocaine, and 0.5 per cent of others. While they are used as a tonic, anodyne, diaphoretic, etc., the major importance is as a source of alkaloids.

Bayberry bark is the dried root bark of a shrub, *Myrica cerifera*, which grows in the eastern United States. It contains resins, gums, starch, etc. Medically it is used as an astringent, alterative, and cholagogue. The same shrub yields bayberry wax from the berries.

Saw-palmetto berries are the dried ripe fruit of the common stemless palm, *Serenoa serrulata*, which grows in the southern part of the United States. The berries are high in fixed and volatile oils. They are a diuretic, sedative, aphrodisiac and pectoral, and a source of **saw-palmetto oleoresin.** A solid extract of the berries, prepared *in vacuo*, is available.

Areca nuts or **betel nuts** grow on a species of palm, *Areca catechu*, native in eastern tropical Asia. The nuts contain alkaloids in addition to tannins and fats. They are sold whole or ground, and used as a teniacide, masticatory and mild astringent. In veterinary medicine they are used as a laxative.

Tamarind is the partially dried fruit of *Tamarindus indica*, preserved in sugar or syrup. The tamarind grows in Africa and the East and West Indies. It is imported from the West Indies. It contains about 10 per cent of tartaric acid and about 8 per cent of potassium bitartrate with sugar, pectin, etc., and is used in medicine as a laxative and refrigerant.

Fishberries or **cocculus** are the dried fruit of an East Indian plant, *Anamirta cocculus*. They contain about 50 per cent of fat and are a sedative and nervine. Industrially they are used as an insecticide. They have been used to arrest fermentation of alcoholic beverages but this use is obsolete. The berries are also used as a fish poison.

Cassia fistula or **cassia pods** are the dried ripe fruit of the tropical drumstick tree. This grows in upper Egypt and in India, and is cultivated in tropical Africa and America. The pods contain a high percentage of sugar, with gums, tannins and hydroxymethyl anthraquinone. This material is not to be confused with cassia, but is used as a laxative. **Cassia pulp** as marketed is from cassia fistula pods.

Arnica flowers are the dried flower heads of *Arnica montana* growing throughout the northern hemisphere. They contain up to 1 per cent of volatile oil, and are a tonic, stimulant, vulneric, febrifuge, diuretic, sternutatory, emmenagogue, nervine and rubefacient. A solid extract, prepared *in vacuo*, is available. **Arnica roots** are from the same source and are used as an antiseptic, alterative, tonic and antipyretic.

Borage flowers are the dried flowers of *Borago officinalis* grown in the Levant, Germany and the United States. They contain potassium nitrate, along with gums and resins and are a diuretic, demulcent and emollient. **Borage leaves** have somewhat similar properties. The fresh leaves are a salad green.

Calendula flowers are the dried flowers of the **marigold family,** *Calendula officinalis*. They are a vulneric, alterative, resolvant, stimulant and diaphoretic. A dried extract, prepared *in vacuo* is available.

Chamomile flowers are the dried flowers of *Anthemis nobilis*, a plant which grows in temperate climates. They contain up to one per cent of volatile oil along with bitter glucoside and other ingredients. Grades sold are Hungarian and Roman. They are used as a carminative, emmenagogue, emetic, stimulant, tonic, diaphoretic and antispasmodic. A solid extract, prepared *in vacuo* is available.

Elder flowers are the dried flowers of the elder shrub, *Sambucus canadensis*. They contain volatile oil, resin, etc. Grades are bright and dark. The flowers are used as a carminative, stimulant, sudorific, diaphoretic and diuretic. A powdered extract, prepared *in vacuo*, is available. **Elder leaves** are used for the preparation of ointments.

Linden flowers are the dried flowers of the linden tree, *Tilia platyphylla* and *Tilia sylvestris*. They are a stimulant, diaphoretic, antispasmodic and tonic. **Linden flowers with leaves** are similarly derived and used.

Malva flowers are the dried flowers of the Eurasian mallow plant, *Malvaceae sylvestris* or *Malvaceae rotundifolia.* Blue and black flowers are sold as well as dried **malva leaves.** They are used in medicine as a demulcent and emollient.

Safflower or **carthamus** consists of the flowers of a variety of saffron, *Carthamus tinctorius.* It grows in the Mediterranean region and in the United States. It is used as an emmenagogue, diaphoretic and astringent.

Grindelia robusta or **gum plant** consists of the dried leaves and flowering tops of an herb growing in the southwestern part of the United States. It contains 20 per cent of resins. Uses are as expectorant, stomachic, diuretic, tonic, antispasmodic and sedative.

Passion-flower herb is the dried flowering and fruiting tops of *Passiflora incarnata,* a plant which grows in the southern part of the United States. It contains a small amount of alkaloid and is used as a nerve sedative and narcotic. A powdered extract, prepared *in vacuo,* is available.

Pulsatilla, meadow anemone or **windflower** is the dried herb of *Pulsatilla vulgaris,* native to temperate regions of Europe and Asia. It is a mydriatic, sedative, anodyne, diaphoretic, emmenagogue, diuretic, emetic, expectorant and vesicant. A solid extract, prepared *in vacuo,* is available.

Rue is a strong-scented European herb, *Ruta graveolens.* It is a stimulant, rubefacient, abortifacient, emmenagogue and nervine.

Broom or **broomtop** consists of the dried tops of the common broom plant, *Cytisus scoparius.* The seeds or flowers are also used. In varying amounts, the product is an emetic, tonic, narcotic, cathartic and diuretic. A solid extract, prepared *in vacuo,* is available.

Clover tops are the dried tops of *Trifolium pratense* growing in the northern hemisphere. They contain resins and tannin and are used as alterative and sedative. A powdered **extract,** prepared *in vacuo,* is available.

Cornsilk or **zea** is the dried styles and stigmas, or silk, of the ear of ordinary Indian corn, *Zea mays*. It is used in medicine as a diuretic, demulcent and alterative. A solid extract, prepared *in vacuo*, is available.

Euphorbia or **snakeweed** is the dried herb of *Euphorbia hirta*, widely distributed in tropical countries. It contains a glucoside and resins and is used as a diuretic, expectorant and antiasthmatic.

Skullcap or **scullcap** is the dried overground portions of *Scutellaria lateriflora*. It grows in North America and is sold as Eastern and Western. It is used in medicine as a tonic, sedative and antispasmodic. A solid extract, prepared *in vacuo*, is available.

Lupulin is the resinous powder obtained from the strobiles of *Humulus lupulus*, which is widely grown. It contains choline, asparagine, wax, etc. Over 60 per cent is ether-soluble. It is an aphrodisiac, stimulant and anodyne.

Kamala consists of the hairs covering the fruit of *Mallotus philippinensis* which grows in China, Australia, India and the Philippines. It is an anthelmintic. A solid extract, prepared *in vacuo*, is available.

Agaric is the dried white body of a fungus growth of *Fomes officinalis*, which develops on various species of *Pinus*. It is an antihydrotic and purgative.

Cantharides or **Spanish flies** consist of dried ground insects, *Cantharis vesicatori*, according to U.S.P. standard. The insects are flattened, 15-25 mm. long, and about 5-8 mm. wide. They are green or blue-green with a metallic luster. The insects contain 0.4-0.8 per cent of cantharidin and some 12 per cent of fat and varied resins. Russian and Chinese grades are sold in whole, or powdered form. They are an aphrodisiac, emmenagogue, rubefacient, vesicant, stimulant and diuretic. Uses are largely external. They are frequently an ingredient of hair tonics.

CHAPTER XXXI

EXTRACTS OF NATURAL PRODUCTS

These extracts are obtained by the simple extraction of naturally occurring products. Each extract has a predominant characteristic but usually contains numerous substances admixed with the active principle. The liquid used for extraction is in most cases water, but may be alcohol in appropriate concentration, aqueous alkalies, etc. In many cases the extracted solution is evaporated to dryness and sold in dry form. Others are viscid liquids. Insoluble matter not removed by filtration is often present.

The predominant tonnage group consists of those products high in tannin content and used as tanning agents. They are usually also used as a source of tannin as a mordant in dyeing. Tanning agents shade into a group of products also having coloring properties. A substantial number of extracts can only be considered as miscellaneous because of diverse uses. Some of these are medicinals. Many minor extracts are mentioned incidentally with their source, in the previous chapter, and do not appear in this chapter.

Quebracho extract is obtained by aqueous extraction from the dried wood or bark of a South American tree, *Aspidosperma quebracho blanco.* Its value depends on the tannin content. Quebracho is sold as a highly viscous liquid or as a brittle solid. The liquid contains 35 per cent of tannins, the solid 63 per cent, and the clarified solid 64 per cent. Medically it is a febrifuge, antispasmodic and tonic. It is used in tanning leather and in dyeing and printing fabrics.

Gambier is the dried aqueous extract from the leaves and twigs of a Malayan woody vine, *Uncaria gambier.* U.S.P. X required not less than 70 per cent solubility in water and 60 per cent in alcohol. The composition is 10-30 per cent catechin, 20-50 per cent catechutannic acid, together with wax, oil, quercitin and gambiercatechu reds. Gambier is sold in common, plantation and Singapore grades. A selected quality is sold as cubes cut from the dried extract. It is an astringent and tonic. Industrially it is used in tanning leather, in dyeing browns and blacks, and in leak-stopping preparations and boiler compounds.

Sumac extract or **sumach extract** is obtained by concentration of an aqueous extraction of the leaves, small twigs, ripe fruit and bark of the sumac tree, *Rhus glabra*. The tree grows in the eastern United States and Europe. The various parts used contain organic acids, gums, etc, in addition to tannins. Grades sold are 42°Tw., 51°Tw. and Sicilian or Italian stainless. Medically it is an antidiarrhetic, refrigerant and tonic. The major use is in tanning leather, and dyeing and printing textiles.

Chestnut extract is the product of the aqueous extraction of the bark of the chestnut tree, of the genus *Castanea*. It grows from Maine to Florida, and in Europe. The value depends on the tannin content. Grades sold are clarified liquid containing 25 per cent of tannin, and powdered solid of 60 per cent tannin. Medically it is a mild sedative, tonic and astringent. The major use is for tanning leather, and as a mordant in dyeing and printing textiles, particularly black silk.

Oakbark extract is prepared by aqueous extraction of the bark of *Quercus robur* or *Quercus alba*, which grow in the eastern United States, Europe and Asia. Major ingredients of the extract are gallic acid, quercitannic acid, etc. It is sold as a concentrated solution containing 25 per cent of tannins and is used largely in tanning fine sole leather.

Quercitron extract is the aqueous extract from the bark of the black oak, *Quercus coccinea,* and is closely allied to oakbark extract. It is sold as a liquid of 51°Tw. and as solid extract, the latter sometimes in different shades of color. The major uses are in tanning, dyeing, and printing leather.

Hemlock extract is obtained by aqueous extraction from the bark of the hemlock, *Tsuga canadensis*. It is sold as a concentrated liquid containing 25 per cent of tannins, and is used mainly for tanning leather, to a lesser extent as a source of tannin for other purposes.

Gall extract or **nutgall extract** is obtained by aqueous extraction from the nutgalls of commerce which develop on various species of oak, genus *Quercus*. The extract is used in tanning leather, in the manufacture of black inks of the so-called iron-gallotannate type—and as a mordant in dyeing and printing textiles.

Wattle bark extract is obtained by the aqueous extraction of wattle bark from *Acacia*. It is high in tannins and is sold as 60°Tw. for use in the tanning of leather, and as a source of tannin for other purposes.

Mangrove extract is obtained by aqueous extraction from mangrove bark, from *Rhizophora mangle*. It is sold of a liquid grade containing 25 per cent of tannin and as solid grade containing 55 per cent. Use is in tanning of leather and for related purposes.

Cutch or **black catechu** is a dried extract from the wood and pods of *Acacia catechu* and from the betel nut of *Areca catechu*. Both are grown in India and nearby localities. The ingredients are 25-35 per cent of catechutannic acid and 2-10 per cent of acatechin quercitin, gums and catechu reds. It is imported from the Philippines, and medically is an astringent and tonic. The major use is as a tanning agent, as a source of tannins in dyeing, and in wood stains and boiler compounds.

Myrobalans extract is obtained by aqueous extraction of *myrobalans* from trees of the genus *Terminalia*. The liquid grade contains 25 per cent of tannins. A 50 per cent solid grade is offered. The products are sometimes further classified as to source. Uses are the same as of other high-tannin extracts.

Divi-divi extract is obtained by aqueous extraction from the fruit divi-divi of a tropical American tree, *Caesal pinia coriaria*. The extract is high in tannic and gallic acids and is sold as containing 25 per cent of tannins for use in tanning leather.

Spruce extract or **spruce-sulfite extract** is obtained as a by-product in the manufacture of pulp from spruce, genus *Picea*. Chemically it is a complex mixture of lignosulfonic acids, or of their alkali and alkaline-earth salts, with unreacted lignin and degradation products. Varied grades are liquid extract, powdered extract and a super extract. It is not a true tanning agent by itself but a semitanning and loading agent used in leather tannage. It has many other uses as adhesive, boiler compound, etc., where an inexpensive organic colloid is required.

Logwood extract is obtained by aqueous extraction of the heartwood of *Hematoxylon campechianum*, a tree growing in Central America and the West Indies. The wood is cut up and sold in the form of small logs, which in turn are reduced to chips for easy extraction. The wood contains about 10 per cent of hematoxylin, which is the active coloring agent, along with tannin, fatty acids, resins, etc. The liquid extract is concentrated to a definite specific gravity *in vacuo*. It is sold at 51°Tw. The solid is obtained when the extract is evaporated completely to dryness. Crystals separate during the process of evaporation and are isolated from the mother liquor as another grade, **logwood crystals.** Medically logwood extract is used as an antidysenteric and antidiarrhetic. The important use is for dyeing textiles and coloring other substances.

Hematin is obtained from logwood extract by adding ammonia and exposing to air. It is an oxidation product of hematoxylin. Liquid of 51°Tw. and hematin crystals are sold, the latter being more important. Hematin gives a bright red color with alkalies and its major use is as a dyestuff.

Fustic extract is obtained by aqueous extraction of the heartwood of a common tropical American tree, *Chlorophora tinctoria* or of *Manchuria tinctoria*. The preparation, properties and uses parallel those of logwood. It is also sold as a liquid, a solid and as crystals.

Irish moss, carageenin or **algin** is the dried, bleached form of a seaweed or kelp, *Chondrus crispus*, or other seaweeds found along the coast of New England and Ireland. Bleaching should be by sun, but is occasionally done with sulfur dioxide. It is prepared as sections 2-5 inches long consisting almost entirely of gum. When boiled in water for some time a colloidal dispersion results which gelatinizes on cooling. It may be precipitated in purified form by alcohol. The extract is sold as ordinary, powdered 80-90 mesh, and bleached prime. It is used as a food, in making jellies and blanc mange, in the treatment of textiles, as a clarifying agent, and medically as a demulcent. Irish moss is sometimes confused with locust-bean extracts described under their source, carob seed.

Pectin is a term for a group of substances which are carbohydrates. They are extractable from ripe fruits and vegetables but commercially are obtained from apples or citrus fruits. Pectins may be prepared as such, or may be liberated by restricted acid or enzymic hydrolysis. Apple pectin is sold as a brown solution, citrus pectin as a white powder precipitated by alcohol from solution. Calcium may be present in combination. The compounds are methylated derivatives which can be further hydrolyzed to pectic acids and methyl alcohol. The aqueous solutions are viscous and solidify to a jelly on adding sugar. Grades are based on the relative strength in "setting" fruit jellies. The formation of such jellies when pectin is not added as such is dependent on the natural pectin content of the ripe fruit.

Osage orange extract is obtained by aqueous extraction from the bark of a native shrub, *Maclura pornifera.* It contains both tannins and a natural dyestuff and is sold in a liquid form of 51°Tw., and as crystals. Both are used for the tanning and coloring of leather and for dyeing textiles.

Brazilwood extract, hypernic extract or **pernambuco extract** is obtained by aqueous extraction from the wood of tropical American trees of the *Caesalpinia* family, the redwood of commerce. The important ingredient is a natural dyestuff, brazilin. It is sold as a 51°Tw. liquid extract, and as a solid, and is used for dyeing red and purple shades of wood, ink, textiles, etc., as well as in the manufacture of red lakes.

Archil extract, orchil extract or **cudbear** is a dyestuff obtained from various species of lichens such as *Rocella tinctoria,* by fermentation followed by the action of air, and extraction with dilute aqua ammonia. The lichens are native to the Mediterranean countries and Eastern islands of that region. The major ingredients are orcin and orcein. Single, double and triple strengths are quoted. Medically the extract is an antiseptic. It is used as a dyestuff for wool and silk in either acid or alkaline baths, or for coloring various foods and medicinal products. The color is somewhat fugitive.

Persian-berry extract is obtained by aqueous extraction of the dried bark of *Rhamnus frangula*. The bush is variously known as **Aleppo buckthorn, Smyrna buckthorn, European buckthorn,** etc. The extract is used mainly for its content of tannin and coloring matter, for coloring leather and textiles. An extract of unripe berries is also sometimes sold and used.

Witch-hazel extract is a dilute alcoholic solution of the distillate from *Hamamelis virginiana* bark, twigs and leaves. The shrub grows in the eastern United States and is collected in the winter months when the twigs are free from sap. The N.F. grade is sold and contains 14 per cent of alcohol. It is used in medicine and pharmacy and as a home remedy for the treatment of bruises, as well as in varied toilet goods.

Bay rum is a fragrant liquid originally prepared in the West Indies by distilling 400 pounds of dried bay leaves with 65 gallons of rum, 100 gallons of water and a little salt. It is now commonly made from oil of myrcia, orange peel oil, and oil of pimenta, in a 57 per cent solution of alcohol. It is used in medicine for its aromatic properties, in cosmetics such as shaving lotions, and as an alcoholic rubbing lotion.

Rose water is an aqueous solution of the odorous substances of the rose, *Rosa gallica,* prepared by steam-distilling the fresh flowers. It is used as a perfume. The usual grade is known as triple distilled.

Pyrethrum extract is a solution of pyrethrins from pyrethrum flowers, *Chrysanthemum cinerarifolium*. The usual solvent is deodorized kerosene although there is some demand for alcoholic extracts. The usual grade is a kerosene solution containing 2.4 per cent of pyrethrins which can be diluted 19:1 with deodorized kerosene to give a liquid insecticide. A 3.6 per cent grade for a dilution of 29:1 is also quoted. Related **derris extracts** and **cubé extracts** for similar purposes are also available but are less widely offered. They contain rotenone as the active agent.

Agar, agar-agar, Japanese isinglass or **Chinese isinglass** is by U.S.P. definition the dried mucilaginous substance extracted from various species of *Gelidium* and closely related algae. Not more than one per cent of foreign organic matter, one per cent of acid-insoluble ash, and 18 per cent of moisture is permissible. It enters the market in the form of thin, adherent translucent strips a few inches long, or ground to a coarse white powder. It contains over 60 per cent of a gelatinous carbohydrate, gelose, and a little protein and pectin. In cold water it forms a mucilaginous or jelly-like mass. It dissolves in hot water and gelatinizes on cooling. Grades sold are numbers 1, 2 and 3 of declining quality and price. Agar is used in culture media, as a laxative, in the East in soups and jellies, in photography, as a substitute for gelatin, as a sizing for textiles, as a thickener for dyes for printing textiles, and in many analogous ways.

Licorice extract is obtained by aqueous extraction from the rhizomes and roots of the licorice plant, varied species of *Glycyrrhiza*. It is evaporated to dryness and sold as a mass in flattened cylindrical rolls or in powdered form. The U.S.P. grade must be sweetish and not more than very slightly acrid. The extract must show over 60 per cent water-solubility and an absence of foreign starches. It is used in medicine as an expectorant, laxative, demulcent and corrigent, as a flavoring agent in candy, tobacco, etc., and as a foam producer in beverages and fire extinguishers. For the major effect as a foam producer **ammoniated licorice extract** is preferable.

Papain, pawpaw juice or **vegetable pepsin** is the active principle of the juice of the green papaya fruit and of the leaves of *Carica papaya*, both from the Far East. It is sold in powdered form after evaporation of the extract. Papain is a proteolytic enzyme intermediate in action between pepsin and trypsin and is used in medicine as a digestant. It is active in acid, neutral or alkaline solution.

Aloin is a crystalline substance, a pentoside or mixture of pentosides according to U.S.P. definition, extracted with alkali from aloes, usually *Curacao* aloes. It is a light to dark yellow, finely crystalline powder, and darkens on exposure to light and air. Aloin varies in solubility, but is quite soluble in water, alcohol or acetone and slightly so in ether. It dissolves in aqua ammonia or aqueous alkalies with a red color. The alkaline solution decomposes rapidly. The ash must not exceed 0.5 per cent. It is a cathartic or purgative.

Chrysarobin is a yellow to brown crystalline mixture of neutral principles obtained by the purification of **Goa powder,** which occurs in the wood of *Vouacapoua araroba.* It turns brown on exposure to air. The crude **araroba** contains 80 per cent of chrysarobin. It is very slightly soluble in water but soluble in alcohol, ether or carbon bisulfide. The U.S.P. material is used in medicine in the treatment of skin diseases.

CHAPTER XXXII

ALKALOIDS AND THEIR SALTS

Alkaloids are normally complex basic organic substances occurring naturally in plants. There are exceptions. Most of them are heterocyclic compounds and contain a tertiary nitrogen atom, as well as carbon, hydrogen and sometimes oxygen. They react with acids by addition to form salts.

Alkaloids always occur as mixtures in plants; opium contains at least 25 different alkaloids. To obtain the alkaloid, the plant material is usually dried, ground and extracted with a suitable solvent. The extract is then distilled *in vacuo* and the distillate acidified and filtered, to separate impurities from the soluble salt of the alkaloid. The alkaloids are then precipitated from the filtrate by making it alkaline, or if water-soluble, they are separated by acidifying and extracting with another solvent, or they may be removed by absorption or by some special method. The natural mixture is separated into its component parts by further extractions, by fractional crystallization, or by both methods.

Most of the alkaloids are used medicinally for their special physiological effect. For example, quinine is a preventative and cure for malaria because of its specific toxicity for malaria protozoa.

Some of the alkaloids are used for other than medicinal purposes, as in the case of the cinchona alkaloids which are employed for the moth-proofing of fabrics. Many of the alkaloids used medicinally have standards of purity set for them by the various pharmacopoeias. The salts have the same physiological action in general as the bases, the alkaloids themselves.

Except in a few cases the alkaloids are white crystalline substances. The free alkaloid base varies in solubility in organic solvents. The salts, such as the hydrochloride and sulfate, are usually water-soluble, and therefore the free bases dissolve in aqueous acids to form the respective salts. Space does not permit giving the melting points, which are usually characteristic. As would be expected from the nature of the sources most alkaloids are very expensive, and many are sold only under very rigid restrictions. As a matter of condensation their physiological action will be given in medical terms. The meanings are indicated in Appendix B.

Morphine, $C_{17}H_{19}O_3N,H_2O$ is the chief alkaloid of opium, constituting 7.5 to 15 per cent of the gum opium. It is a complex derivative of phenanthrene. **Morphine acetate, morphine ethyl hydrochloride, morphine hydrobromide** and **morphine sulfate** are prepared from the alkaloid and sold commercially. Other salts are less common. The U.S.P. product is the sulfate, $(C_{17}H_{19}O_3N)_2H_2SO_4,5H_2O$. The standard requires negligible ash and not more than 12 per cent of combined water. The salts are moderately soluble in water. The free base is soluble in acids and but slightly soluble in organic solvents such as alcohol, chloroform and ether. Morphine is administered as a narcotic, sedative, hypnotic and anodyne.

Apomorphine, $C_{17}H_{17}O_2N$, is a white crystalline substance obtained as the hydrochloride by heating morphine with hydrochloric acid in sealed tubes, to dehydrate it. **Apomorphine hydrochloride** is a U.S.P. product, $C_{17}H_{17}O_2N,HCl,\frac{1}{2}H_2O$. It is slightly soluble in water, alcohol, chloroform or ether. The aqueous solutions turn green on exposure to air, unless acidified. Its medical uses are as a cardiac depressant, emetic, expectorant, sedative and hypnotic.

Codeine, $C_{18}H_{21}O_3N,H_2O$, is an alkaloid obtained from opium. It is also prepared by the methylation of morphine. The U.S.P. standard for the alkaloid requires not more than six per cent of combined water, and negligible ash. **Codeine phosphate** and **codeine sulfate** are formed by reaction with the respective acids. The U.S.P. standard requires that the phosphate, $C_{18}H_{21}O_3N,H_3PO_4,1\frac{1}{2}H_2O$, contain not less than 70 per cent of anhydrous alkaloid. Codeine sulfate, $(C_{18}H_{21}O_3N)_2$-$H_2SO_4,5H_2O$ is also a U.S.P. product and must have negligible ash and not over 12 per cent of combined water. **Codeine hydrochloride,** $C_{18}H_{21}O_3N,HCl,2H_2O$, is similarly formed but is not U.S.P. The alkaloid base is slightly soluble in water, extremely soluble in alcohol and very soluble in ether. The salts are extremely soluble in water and almost insoluble in organic solvents. Codeine is used as the free alkaloid, or preferably as the phosphate, as an analgesic, hypnotic and sedative, particularly in cases of mental disorders.

Cocaine, $C_{17}H_{21}O_4N$, is the alkaloid obtained from cocoa leaves, various varieties of erythoxylon. Both the alkaloid and **cocaine hydrochloride,** $C_{17}H_{21}O_4N,HCl$, have U.S.P. standards requiring negligible ash. Cocaine is practically insoluble in water but is very soluble in alcohol or ether, and extremely soluble in chloroform. The hydrochloride is extremely soluble in water, very soluble in chloroform, and moderately soluble in alcohol. It is used as a local anesthetic, usually as the hydrochloride, but is being replaced by such synthetic compounds as procaine. Other uses are as a stimulant, sedative, antisialagogue, mydriatic, anodyne, antihydrotic and antipruritic.

Strychnine, $C_{21}H_{22}N_2O_2$, is a very poisonous alkaloid obtained from the various plants of the genus *Strychnos,* as from nux vomica. It is a tertiary base, moderately soluble in chloroform, slightly so in benzene. Crystalline and powdered forms are available. Salts sold are **strychnine acetate, strychnine arsenate, strychnine arsenite, strychnine glycerophosphate, strychnine hydrochloride, strychnine hypophosphite, strychnine nitrate, strychnine phosphate** and **strychnine sulfate.** Of these, the U.S.P. specifies that the nitrate, $C_{21}H_{22}O_2N_2,HNO_3$, shall not have over 0.1 per cent ash, and the sulfate, $(C_{21}H_{22}O_2N_2)_2,H_2SO_4.5H_2O$, not over 11.5 per cent of combined water. The U.S.P. salts are only moderately soluble in water or alcohol. Strychnine is used as a tonic to stimulate the central nervous system and as stomachic, stimulant, spinant and excitomotor. Unlike most alkaloids it has important uses other than in medicine, primarily as the active ingredient of poisons for mice, rats and other rodents.

Lobeline, $C_{21}H_{23}O_2N$, is a poisonous alkaloid obtained by extraction from the seeds or leaves of the plant, *Lobelia.* The yellowy, sirupy liquid is soluble in water and readily soluble in alcohol, ether or chloroform. It is used to treat paralysis of the respiratory centers, intoxications and narcosis.

Brucine, $C_{23}H_{26}O_4N_2,2H_2O$, is obtained from the seeds of nux vomica and ignatia. It is soluble in alcohol, chloroform or ether. The alkaloid and **brucine sulfate,** $(C_{23}H_{26}O_4N_2)_2,H_2SO_4,7H_2O$, are among the few inexpensive alkaloids. The sulfate is soluble in water and alcohol. In medicine its action is similar to that of strychnine but milder. It is not a U.S.P. product. Brucine is also used as a denaturant for specially denatured alcohols.

Quinine, $C_{20}H_{24}O_2N_2,3H_2O$, is a white crystalline alkaloid extracted from cinchona bark or "Peruvian bark." It is a derivative of quinoline and quinuclidine, is dibasic and forms two series of salts. The free base is extremely soluble in alcohol or chloroform. The alkaloid is an important U.S.P. product, of a grade containing not over 0.1 per cent ash. U.S.P. derivatives are **quinine ethylcarbonate** or **euquinine,** $C_{23}H_{28}O_4N_2$; **quinine bisulfate,** $C_{20}H_{24}O_2N_2,H_2SO_4,7H_2O$; **quinine sulfate,** $(C_{20}H_{24}O_2N_2)_2,H_2SO_4,2H_2O$; and **quinine dihydrochloride,** $C_{20}H_{24}O_2N_2,2HCl$. Euquinine is very soluble in alcohol, ether or chloroform. The bisulfate is very soluble in water, moderately so in alcohol. The sulfate is but slightly soluble, even in water. The dihydrochloride is extremely soluble in water and moderately so in alcohol. The salts of the alkaloid are used as a tonic, emmenagogue, antiperiodic, antiseptic and antipyretic. Self-administration for prevention or control of fever in tropical regions is common. Non-U.S.P. salts sold are **quinine acetate, quinine arsenate, quinine arsenite, quinine citrate, quinine dihydrobromide, quinine ferrocyanide, quinine formate, quinine glycerophosphate, quinine hydrochloride, quinine hydrochlorosulfate, quinine hydroiodide, quinine hypophosphite, quinine phosphate, quinine salicylate, quinine sulfocarbolate, quinine tannate, quinine tartrate** and **quinine valerate.** Their uses are also medicinal.

Quinine-urea hydrochloride, $C_{20}H_{24}O_2N_2,HCl,CO(NH_2)_2,HCl,5H_2O$, is prepared by heating quinine hydrochloride with urea. It must contain between 58 and 65 per cent of anhydrous quinine to meet the U.S.P. standard. This derivative is extremely soluble in water, and very soluble in alcohol. The compound is used as an anesthetic and hemostatic by injection.

Quinidine or **chinidine,** $C_{20}H_{24}O_2N_2$, **is a** colorless crystalline alkaloid isomeric with quinine and obtained from various species of *Cinchona.* It is marketed as large or small crystals, or powder. **Quinidine sulfate,** $(C_{20}H_{24}O_2N_2),H_2SO_4,2H_2O$, is made by reaction with sulfuric acid and is a U.S.P. product. The ash must not exceed 0.1 per cent and the combined moisture must be under five per cent. The alkaloid is moderately soluble in alcohol or ether and extremely soluble in chloroform. The sulfate is only slightly soluble in cold water but very soluble in alcohol or chloroform. These products are used as an antiperiodic, tonic, antiseptic and antipyretic, their action being similar to that of quinine but weaker.

Cinchonine, $C_{19}H_{22}ON_2$, is an alkaloid from cinchona bark. It is slightly soluble in alcohol or ether. The commercial product is sold as large crystals, small crystals or powder. Medically it is a bitter tonic and antiperiodic. Industrially it is used as a mothproofing agent, particularly in the form of the oleate. Many salts are sold of which **cinchonine sulfate,** $(C_{19}H_{22}ON_2)_2$-H_2SO_4, is the most important. The sulfate is used medically in the same way as the alkaloid, and is preferable because of substantial solubility in water or alcohol.

Cinchonidine, $C_{19}H_{22}ON_2$, is another alkaloid extracted from cinchona bark. Structurally it is *alpha*-quinidine. It is moderately soluble in alcohol, and is sold as large or small crystals, or powder. **Cinchonidine sulfate,** $(C_{19}H_{22}ON_2)_2,H_2SO_4,3H_2O$, is a U.S.P. X and N.F. product. The alkaloid is moderately soluble in alcohol. The sulfate is slightly soluble in water or alcohol. Medically it is used as a tonic and antiperiodic, industrially in moth-repellent preparations. It is substantially more expensive than cinchonine.

Emetine hydrochloride, $C_{29}H_{40}O_4N_2,2HCl$, is the reaction product of hydrochloric acid with emetine, obtained from ipecac root or prepared synthetically. The U.S.P. standard requires negligible ash, and a loss of between 8 and 16 per cent on drying at 100° C. The hydrochloride is very soluble in water or alcohol. The free alkaloid is a brown resin but is not usually offered. The hydrochloride is used as an emetic, expectorant, antipyretic, and as a specific for amoebic dysentery.

Dover's powder or **powder of ipecac and opium** is a diluted mixture of ipecac and opium. The U.S.P. grade contains 10 per cent of finely powdered ipecac, 10 per cent of finely powdered opium and 80 per cent of coarsely powdered lactose. It is gray to brown in color. The British preparation replaces the lactose with potassium sulfate. It is used as an anodyne and diaphoretic.

Homatropine hydrobromide, $C_{16}H_{21}O_3N,HBr$, is a very poisonous white crystalline compound, soluble in chloroform or alcohol and very soluble in water. It is prepared from hydrobromic acid and **homatropine,** which is a synthetic alkaloid prepared from tropine and mandelic acid. The U.S.P. standard requires negligible ash. The salt is used medicinally as a mydriatic.

Ephedrine, $C_{10}H_{15}ON$, is an alkaloid obtained by extracting the leaves of *Ephedra*, the Chinese mahuang, or by synthetic production. **Ephedrine hydrochloride,** $C_{10}H_{15}ON.HCl$, and **ephedrine sulfate,** $(C_{10}H_{15}ON)_2,H_2SO_4$, are formed by reaction with the respective acids. The sulfate is sold in crystalline and powdered forms. The U.S.P. alkaloid must have a negligible ash; the sulfate contains 75.5-77.3 per cent of the anhydrous alkaloid, the hydrochloride 80-82.5 per cent of anhydrous alkaloid. The alkaloid is an unctuous, very light-colored solid, usually noncrystalline. It is soluble in alcohol, chloroform, ether or fixed oils. The aqueous solution is quite strongly alkaline. The salts are soluble in water or alcohol. The alkaloid is used for treatment of hay fever, asthma, circulatory failure and narcotic poisoning.

Hyoscine hydrobromide or **scopolamine hydrobromide,** $C_{17}H_{21}O_4N.HBr.3H_2O$, is prepared by the reaction of hydrobromic acid and **hyoscine** or **scopolamine,** obtained from the roots of herbs of the genera *Solanaceae*. It is a U.S.P. product, having a negligible ash and not more than 13 per cent of water. The compound is extremely soluble in water, moderately so in alcohol. It is used as a mydriatic, hypnotic and sedative.

Hyoscyamine, $C_{17}H_{23}O_3N$, is an alkaloid obtained from henbane, belladonna and other solanaceous plants. **Hyoscyamine hydrobromide,** $C_{17}H_{23}O_3N,HBr$, and **hyoscyamine sulfate,**

$(C_{17}H_{23}O_3N)_2,H_2SO_4,2H_2O$, are prepared from the alkaloid. The alkaloid is soluble in alcohol, chloroform or ether, slightly so in water. The salts are extremely soluble in water and moderately so in alcohol. The hydrobromide was in U.S.P. X and several preparations in U.S.P. XI contain hyoscyamine. The alkaloid or its salts may be used as a hypnotic, sedative, and locally as a mydriatic.

Duboisine, $C_{17}H_{23}O_3N$, is an alkaloid obtained from the leaves of *Duboisa myoperiodic*, an Australian shrub. It is identical in constitution with hyoscyamine. The commercial salt is **duboisine sulfate,** $(C_{17}H_{23}O_3N)_2,H_2SO_4,2H_2O$. The alkaloid is soluble in alcohol, ether or chloroform, the sulfate in water or alcohol. The alkaloid is a sedative, mydriatic and hypnotic but is not supplied topically because it is insoluble. The sulfate is used as a mydriatic, dilating the pupil of the eye much more powerfully than atropine.

Atropine, $C_{17}H_{23}O_3N$, is the poisonous crystalline alkaloid extracted from the leaves and roots of *Atropa belladonna,* often referred to as **deadly nightshade.** It also occurs in some other plants. **Atropine sulfate,** $(C_{17}H_{23}O_3N)_2,H_2SO_4,H_2O$, is the common salt. The alkaloid is extremely soluble in alcohol or chloroform, moderately so in ether. The sulfate is extremely soluble in water and very soluble in alcohol. Both are U.S.P. products, the alkaloid melting at 114-116° C.; the sulfate not below 188° C. They are used as antispasmodic, stimulant, antihydrotic, antisialagogue, analgesic and mydriatic. The best-known use is application to the eye for dilation of the pupil.

Eserine or **physostigmine,** $C_{15}H_{21}O_2N_3$, is an alkaloid obtained from the dried seeds of *Physostigma venenosum* or the calabar bean of West Africa. The colorless hygroscopic crystals turn red and resinify on exposure to air. The alkaloid is used for preparing **eserine salicylate** or **physostigmine salicylate,** $C_{15}H_{21}O_2N_3,C_7H_6O_3$. This is a U.S.P. product having a negligible ash. **Eserine sulfate** or **physostigmine sulfate** is also sold. The salts are white or yellowish and turn red on exposure to light. A red salt or red solutions have deteriorated in physiological effect. The alkaloid is soluble in alcohol, benzene, ether or chloroform. The salts are soluble in water, alcohol, chloroform or ether, to varying degrees. The alkaloid and its salts are used as a sedative, antineuralgic, diaphoretic, depressant, purgative, myotic, sialagogue and antitetanic. The sulfate is a veterinary remedy for colic and chronic gastric catarrh. The alcoholic extract contracts the pupil of the eye to overcome the effects of atropine.

Hydrastine, $C_{21}H_{21}O_6N$, is a crystalline nonpoisonous alkaloid found in the rootstock of goldenseal and prepared synthetically. **Hydrastine hydrochloride,** $C_{21}H_{21}O_6N,HCl$, and **hydrastine sulfate,** $(C_{21}H_{21}O_6N)_2,H_2SO_4$, are the commercial salts. The alkaloid is slightly soluble in water, alcohol, chloroform or ether, and very soluble in benzene. The salts are very soluble in water or alcohol. Both the sulfate and the hydrochloride are hygroscopic. The alkaloid and its salts are used as an antiseptic, astringent, hemostatic, tonic, alterative and emmenagogue.

Aconitine is an alkaloid obtained from the roots and leaves of *Aconitum napellus.* The amorphous form is an impure mixture of alkaloids, the crystalline form is $C_{34}H_{47}O_{11}N$. The alkaloid is extremely poisonous, and is soluble in alcohol or benzene. Aconitine is used as a diuretic, sudorific, antineuralgic and external anesthetic.

Pilocarpine, $C_{11}H_{16}O_2N_2$, is a colorless to yellow liquid obtained from the dried leaves of two varieties of *Pilocarpus.* **Pilocarpine nitrate,** $C_{11}H_{16}O_2N_2,HNO_3$, is a U.S.P. crystalline salt very soluble in water, moderately soluble in alcohol, and having a negligible ash. **Pilocarpine hydrochloride,** $C_{11}H_{16}O_2N_2,HCl$, is a hygroscopic salt extremely soluble in water or alcohol. Both salts are used medicinally as a diuretic, sialagogue, galactagogue, myotic and diaphoretic.

Sparteine, $C_{15}H_{26}N_2$, is a yellowish, sirupy liquid extracted from the tops of the common broom. It is soluble in alcohol, chloroform or ether. **Sparteine sulfate,** $C_{15}H_{26}N_2,H_2SO_4,5H_2O$, is the crystalline commercial form, very soluble in water or alcohol. It is used as a heart stimulant and diuretic.

Berberine, $C_{20}H_{17}O_4N$, is the alkaloid extracted from the roots of the barberry and related plants. It is soluble in water and forms yellow crystals. **Berberine bisulfate,** $C_{20}H_{17}O_4N,$-

H_2SO_4, **berberine sulfate,** $(C_{20}H_{17}O_4N)_2,H_2SO_4$, and **berberine hydrochloride,** $C_{20}H_{17}O_4N,HCl$, are commercial yellow crystalline salts. The bisulfate is often incorrectly called berberine sulfate. The bisulfate, sulfate and hydrochloride are slightly soluble in water. These salts are used in medicine as a tonic, antiperiodic and stomachic.

Colchicine, $C_{22}H_{25}O_6N$, is a very poisonous yellow alkaloid extracted from the seed of *Colchium autumnale* or meadow saffron. It is a U.S.P. product having a negligible ash. Colchicine is moderately soluble in water, very soluble in chloroform or alcohol. Its uses are as an antirheumatic, antineuralgic, and antipodagric.

Yohimbine, $C_{21}H_{26}O_3N_2$, is an alkaloid obtained from *Yohimbé* bark. The usual salt is **yohimbine hydrochloride,** $C_{21}H_{26}O_3N_2,HCl$. It is water-soluble, and used as an aphrodisiac.

Arecoline, $C_8H_{13}O_2N$, is an alkaloid obtained from the *Areca catechu* or betel nut. The usual compound is **arecoline hydrobromide,** $C_8H_{13}O_2N,HBr$, soluble in water or hot alcohol. The salt is used as a cathartic, sialagogue, myotic and anthelmintic. It is also used in veterinary medicine.

Nicotine, $C_{10}H_{14}N_2$, is obtained from tobacco leaves, is a derivative of both pyridine and pyrrolidine, and is a colorless to yellow, oily liquid. It turns brown on exposure to air and is very soluble in water, alcohol, ether, chloroform, oils, etc. **Nicotine sulfate,** $C_{10}H_{14}N_2,H_2SO_4$, is a white crystalline compound derived from nicotine. It is sold as a solution in water, containing 40 per cent of nicotine. Nicotine is a local irritant but the major use is as an agricultural insecticide.

Caffeine, $C_8H_{10}O_2N_4,H_2O$, is the alkaloid obtained from coffee, tea, guarana, and kola nuts. It is also prepared synthetically. The white crystalline alkaloid is 1,3,7-trimethyl xanthine. It is moderately soluble in water, alcohol or acetone, very soluble in chloroform. The U.S.P. standard requires not over 0.05 per cent of ash nor over 9 per cent of combined moisture. Medicinally it is used as a cerebral and muscular stimulant or diuretic. Much is present in compound form in stimulating beverages. **Caffeine hydrobromide,** $C_8H_{10}O_2N_4,HBr,$-

$2H_2O$, sometimes called **caffeine bromide,** is somewhat soluble in water or alcohol. It is used mainly as a diuretic. **Citrated caffeine** is a mixture of caffeine and citric acid which according to U.S.P. standards contains 48-52 per cent of anhydrous caffeine. The ash must not be more than 0.1 per cent. Its uses are similar to those of the alkaloid. **Caffeine with sodium benzoate** is a U.S.P. mixture of caffeine and sodium benzoate. When dried at 80° C. it must not lose more than 5 per cent of combined moisture. The anhydrous material must contain 47-50 per cent of anhydrous caffeine and 50-53 per cent of sodium benzoate. It is used for the same purposes as caffeine.

Theobromine, $C_7H_8O_2N_4$, is obtained from the seeds of the *Theobroma cacao*, or cacao bean, in which it is the principal alkaloid. It also occurs in small amounts in the kola nut and in tea, and can be synthesized. The structure is 3,7-dimethyl xanthine. It is soluble in organic solvents, but only slightly soluble in water, and is used as a nerve stimulant and diuretic. Theobromine with sodium salicylate or **theobromine sodiosalicylate** is a U.S.P. material prepared by combining the sodium salt of theobromine with sodium salicylate in approximately molecular proportions. When dried at 110° C. it contains not less than 46.5 per cent of theobromine and 35 per cent of salicylic acid. It decomposes on exposure. Use is largely as a diuretic.

CHAPTER XXXIII

ESSENTIAL OILS AND OLEORESINS

Essential oils are volatile or ethereal, odorous bodies of an oily nature, obtained from the flowers, leaves, bark, seeds or roots of a great number of trees and plants. Essential oils vary greatly among themselves as to constitution, and usually contain a number of compounds such as hydrocarbons, particularly terpenes, alcohols, aldehydes, ketones, esters, etc., in varying proportions and combinations. They are not chemical compounds but mixtures of natural origin.

Similarly, any synthetic odor is composed of a complex mixture. To illustrate, **rose odors** may contain citronellol, geraniol, phenylethyl alcohol, ionone, benzophenone, citronellyl acetate, geranyl acetate, hydroxycitronellol, phenylacetic acid, etc. Similarly **jasmine odors** may contain benzyl acetate, hydroxycitronellol, linalool, linalyl acetate, phenylethyl alcohol, *alpha*-amyl cinnamic aldehyde, hexyl cinnamic aldehyde, methyl anthranilate, amyl acetate, ionone, musk, phenylacetic acid, etc. **Lily-of-the-valley odors** may contain hydroxycitronellol, phenylethyl alcohol, heliotropine, rhodinol, citronellol, linalool, linalyl acetate, terpineol, geraniol, cinnamyl acetate, musk, etc. **Lilac odors** may contain terpineol, phenylethyl alcohol, cinnamic alcohol, hydroxycitronellol, musk, etc. **Violet odors** may contain ionone, methyl ionone, hydroxycitronellol, phenylethyl alcohol, methyl heptine carbonate, terpineol, heliotropin, benzyl acetate, etc. **Lavender odors** may contain geraniol, linalyl acetate, terpinyl acetate, geranyl acetate, coumarin, benzophenone, hydroxycitronellol, ionone, musk, etc. These are by no means complete lists but serve to illustrate the types of materials which enter into the synthetic mixtures known as perfumes.

Essential oils from the same source are usually more or less uniform in composition, and are identified by physical constants such as specific gravity, refractive index, specific rotatory power, and possibly solubility in selected solvents. To conserve space the specific gravities and refractive indices of many of the essential oils have been assembled in the table at the end of this chapter.

Many of these oils occur in nature in very small quantities and involve a huge amount of labor in obtaining and isolating them. Such oils are naturally very expensive. Sometimes the more expensive oils are adulterated with cheaper oils or with synthetic products bearing some resemblance to the original oil. For example, palmarosa oil may be adulterated with coconut oil, cedar oil, turpentine or even kerosene. The original oil is soluble in 70 per cent alcohol, while the adulterated oil is not. Another example is the adulteration of bitter almond oil with synthetic benzaldehyde. Some essential oils are approximately matched in odor and many other properties by synthetic mixtures of ingredients. Oleoresins are semisolid rather than liquid but otherwise are of the same general type as essential oils.

Essential oils are obtained by a number of methods, according to the nature of the odorous material. Some are distilled with steam from the macerated flowers or other plant material. This does not recover all odorous constituents completely, so that the odor of the oil which separates as a layer in the distillate does not duplicate exactly the odor of the original natural product. This is because some of the ingredients are too high-boiling to distil over, while others may be decomposed at the distillation temperature. Other oils, especially citrus oils, are obtained by expression of the fruit or plant material. This method avoids the destructive effect of the high temperature in steam distillation.

Still another and even gentler method is the enfleurage process in which an odorless fat such as lard or tallow is spread out in a thin layer and the fresh flowers scattered over it. The perfume material which volatilizes from the flowers is absorbed by the fat and later separated from it by washing with alcohol. Again the recovered material is not the same as that in the original flowers, as the fats themselves yield some alcohol-soluble constituents. Materials which can stand more severe action are sometimes mixed with melted fat and the latter filtered off. The perfumed oil or fat is called **pomade.**

Odorous materials are also directly extracted with volatile solvents such as carbon tetrachloride or petroleum ether and the solvent distilled off *in vacuo.* Plant resins, waxes and coloring matter remain mixed in with the essential oils as impurities. Essential oils are as a rule soluble in alcohol, and also in the usual fat solvents such as ethyl ether, petroleum ether, chloroform, carbon tetrachloride, carbon bisulfide, etc.

The yield of flower oils varies greatly with the species and also from season to season. Essential oils are sometimes described as "terpeneless," indicating that they have been treated to remove **terpenes.** Most distilled natural oils contain terpenes. These consist of a series of isomeric hydrocarbon compounds having the general formula $C_{10}H_{16}$, some of them cyclic. Individual terpenes are usually named with an "ene" ending, such as pinene, limoene, etc. These compounds are low in odor value and for this and other reasons detract from the value of an oil containing them. They tend to take up oxygen from the air and thus thicken the oil, also to turn rancid. Terpeneless oils are therefore more concentrated and better in quality than those which retain the terpenes. Essential oils from flowers are often called **floral essences** or **floressences. Perfumes** are normally solutions of complex mixtures of odorous essential oils in alcohol, of greater or lesser concentration. **Flavors** similarly are flavoring types of essential oils or extractives in alcohol. **Nonalcoholic flavors** substitute glycerine as the solvent.

In the following list the oils are classed as far as possible by composition, bringing those intimately related in reasonably close juxtaposition. The same sequence has been followed in the table of physical constants. The order of major constituents is in general, alcohols, aldehydes, ketones, esters, terpenes. More complete data on many of the oils can be obtained from a chemical handbook. Since terminology commonly includes forms such as oil of rose and rose oil as equivalents, no attempt has been made to repeat the two similar forms.

Bois de rose oil is obtained by distillation of varieties of rosewood grown in Cayenne and in Brazil, usually *Aniba po-*

murensis. The colorless oil is quoted as of Cayenne and Brazilian grades, of which the latter is much less expensive. It is used in perfumery for its odor of linalool.

Rosewood oil is a thick yellowish essential oil distilled from varieties of rosewood. Bois de rose oil is a variety of oil of rosewood. **Rhodium oil** is a term also applied to rosewood oil. True rhodium oil is that from the true rhodium shrubs, *Convolvulus scoparius* and *Convolvulus virgatus*. Commercially **imitation rhodium oil** is better known, and consists of a mixture of rose, geranium, cedarwood and sandalwood oils. All are used as perfume oils.

Linaloe-wood oil or **linaloa-wood oil** is distilled from a fragrant wood, *Bursera aloexylon*, which grows in French Guiana, or from another type, *Bursera graveolens*, which grows in Mexico. Both kinds contain linalool, geraniol and terpineol. The Mexican oil also contains methyl heptanone. The colorless oil is used in perfumery.

Coriander-seed oil is an expensive oil distilled with steam from the dried ripe fruit of a European herb, *Coriandrum sativum*. The colorless to pale yellow oil has a distinctive odor and spicy taste. It contains linalool, pinene and cymol, and is used in flavoring materials. It is a U.S.P. product, soluble in 3 volumes of 70 per cent alcohol.

Costus oil is a fragrant oil distilled from the root of an herb, *Saussurea lappa*, found in Kashmir. It is extremely expensive and used in perfumes and sachets.

Ylang ylang oil is distilled from the flowers of *Cananga odorata*, from different localities. It contains linalool, geraniol and esters of these, pinene, and small amounts of numerous other constituents, including the methyl ether of *p*-cresol, which is a powerful and characteristic odorant in this oil. **Manila ylang ylang oil** is the first and most delicately scented fraction which distils over, the latter fractions being sold as **cananga oil or kananga oil.** This is also offered in a rectified grade. **Bourbon ylang ylang oil** is an intermediate quality, also offered in a rectified grade. **Madagascar ylang ylang oil** is another grade. The separation is based merely on odor. The properties of the grades vary considerably, according to the fractions distilled. The color is yellow. The varied kinds are used in medicine and in perfumery.

Canada snakeroot oil is distilled from the root-like stems and the roots of *Asarum canadense.* It contains linalool, pinene, borneol, terpineol, geraniol and methyl eugenol. The yellow-brown oil is used in perfumery.

Origanum oil or **wild marjorum oil** is obtained from various species of marjorum indigenous to the Mediterraneum countries, mainly *Origanum vulgare* or *Origanum creticum.* The physical constants vary according to the origin. The yellow oil darkens on exposure to the air. It has a thyme-like odor, and thyme oil is sometimes sold under the name of origanum. Origanum oil contains carvacrol and cymol. The Triest oil also contains thymol; the Smyrna oil also phenol, linalool and cedrol. Spanish origanum oil is available and is used in flavoring materials and medicinally. An imitation oil is also sold.

Patchouli oil is distilled from the leaves of an East Indian shrubby mint, *Pogostemon patchouli.* The thick brownish yellow oil has a fragrance which improves with age. It contains patchouly alcohol, eugenol and'cinnamic aldehyde, and is used in perfumes. Singapore and domestic grades are quoted, as well as an imitation which is not radically less expensive than the true oil.

Lovage oil is a very expensive perfume oil with a characteristic odor. The colorless oil dissolves in the common organic solvents. It is distilled from various parts of *Levisticum officinale,* or **sea parsley,** which grows in southern Europe.

Ambrette-seed oil is a yellow oil of a musk-like odor obtained by distillation from the seed of a species of abelmosk resembling millett, and known as amber seed or ambrette seed. It is a very expensive perfume oil available in various qualities, depending on the extent to which fatty acids have been removed.

Sandalwood oil is distilled with steam from the wood of the semitropical tree, *Santalum album.* The yellow oil is sold as East Indian, U.S.P., West Indian and Australian. **East Indian sandalwood oil** contains santal alcohols and their esters and santalol. **West Indian sandalwood oil** contains 27-55 per cent of amyrol and cadinene. **Australian sandalwood oil** contains

95-96 per cent of santalol. The U.S.P. grade yields not less than 90 per cent of alcohols calculated as santalol. The West Indian oil thus differs substantially from the other varieties of oil of sandalwood and is known as **amyris oil** to differentiate it. It is somewhat less expensive.

Wormseed oil is distilled in America from the seeds and leaves of the plant *Chenopodium ambrosioides,* and in the Levant from *Artemisia maritima.* The American oil is also known as **chenopodium oil.** The American oil contains ascaridol, *p*-cymol and *l*-limonene; the Levant oil cineol, pinene, terpenes, terpineol and sesquiterpenes. The colorless to yellow oil has a disagreeable odor and a burning taste. The U.S.P. grade contains not less than 60 per cent and not more than 80 per cent of a fraction soluble in acetic acid. It is used in medicine.

Anise oil or **aniseseed oil** is obtained by distillation with steam from the dried ripe fruit of *Pimpinella anisum* or *Illicium verum.* It is U.S.P. and contains anethol and methyl chavicol. The natural oil is sold as a lead-free U.S.P. grade soluble in 3 volumes of 90 per cent alcohol, and is used in medicine, liqueurs and perfumes. Chinese and Russian grades are quoted.

Tarragon oil or **estragon oil** is distilled from a flowering herb, *Artemesia dracuriculus.* It contains substantial amounts of methyl chavicol and has an anise-like odor. The colorless to light yellow or greenish oil is used largely as a flavoring material.

Sage oil or salvia oil is a yellow to greenish oil distilled from the leaves of *Salvia officinalis.* It contains cineol, pinene and thujone, has a sage odor and is used mainly in flavors. Dalmatian and Spanish types are offered.

Fennel-seed oil or **fennel oil** is distilled with steam from the dried fruit of *Foeniculum vulgare* or sweet fennel. It is a U.S.P. product soluble in 1 volume of 90 per cent alcohol. The colorless to pale yellow oil has a bitter taste. It varies according to source and may contain anethol, fenchone, pinene, camphene, phellandrene and dipentene. It is used in medicine, perfumes and in making liqueurs.

Peppermint oil is distilled from the fresh leaves and flowers of the peppermint plant, *Mentha piperita*. The colorless to yellow oil darkens on exposure to air. It has a strong odor and taste of peppermint, and contains among its many constituents menthol and related compounds, pinene, cineol, phellandrene, limonene and cadinene. The U.S.P. grade contains not less than 5 per cent of esters, calculated as menthyl acetate, and not less than 50 per cent of total menthol, free and as esters. Grades sold are natural, redistilled and triple distilled, as well as a terpeneless grade of double strength. Peppermint oil is an antiseptic and anesthetic because of its menthol content. It is widely used as a flavor and odorant and to a minor extent medicinally.

Citronella oil is distilled from a grass such as *Cymbopogon nardus* grown in India, Java and other tropical countries. Important constituents are geraniol and citronellol, each of which may be present in amounts varying from 25 to 45 per cent. It is an important source of these materials. Grades sold are from Ceylon and from Java. The yellow oil has a pleasant odor and is used as a liniment, in medicine, as a perfume, particularly in soaps, and as an insect repellent.

Geranium oil or **rose geranium oil** is distilled from the herb of a number of species of *Pelargonium*. The yellow to green liquid has a pleasant rose-like odor and contains geraniol and citronellol and their esters. Grades sold are Algerian rose and Bourbon. French geranium oil is much more expensive. The natural oil is used very widely in perfumery, as is also a synthetic grade. Terpeneless geranium oil is of about double strength. A special, expensive grade is distilled with rose petals.

Rose oil, attar of roses or **otto of roses** is obtained by steam distillation or by enfleurage from rose flowers. The oil may be red, yellow or green according to its source, which also affects its odor. The natural oil contains 66-75 per cent of geraniol, 24-37 per cent of citronellol and 17-21 per cent of stearoptene. The best quality is from *Rosa damascena*. **Absolute rose oil is extremely expensive.** Lower-quality oils are sold as **rose-**

flower oil. **Imitation rose oil** is also offered. Rose oil is widely used for perfumes, rose water, etc.

'**Palmarosa oil** is distilled from a grass and is known as **Turkish geranium oil.** The colorless to yellow oil has a rose-like odor and occasionally is colored green by the presence of copper. It contains geraniol, geranyl acetate and capronate, and dipentene. It is less expensive than Algerian or Bourbon geranium oil and is used in perfumery.

Cajeput oil or **cajuput oil** is obtained by distillation of the fresh leaves and twigs of a species of East Indian tree. It contains 50-60 per cent of cineol. The technical grade is green, the rectified product sold as U.S.P. X is yellow to colorless and soluble in 1 volume of 80 per cent alcohol. It is miscible with 95 per cent alcohol or ether, and is used in medicine and as an odorant.

Eucalyptus oil is distilled with steam from the fresh leaves of the various species of Eucalyptus trees such as *Eucalyptus globulus.* The commercial oil is colorless or pale yellow and comes mostly from Australia. Its composition varies with the source, but in addition to eucalyptol, as a rule it contains cineol and pinene, and sometimes phellandrene, aromadendrol, and various other constituents. The U.S.P. grade contains not less than 70 per cent of eucalyptol. The oil is quoted on a basis of eucalyptol content as 70 per cent, 80 per cent, etc. It is used in medicine, in perfumes and as an odorant in industrial products.

Savin oil is distilled from the fresh leaves and twigs of the evergreen shrub *Juniperus sabina.* It contains sabinol, cadinene, sabinene and cintronellol. The colorless to pale yellow oil is used in medicine.

Thyme oil is distilled from various species of thyme and varies in properties according to the country from which it comes. Oil from wild thyme is colorless or golden yellow. The red is the French oil. Thyme oil is often adulterated with turpentine, which lowers the specific gravity. **French thyme oil** and **German thyme oil** contain thymol, carvacrol, linalool, borneol, cymol and *l*-pinene. **Wild thyme oil** contains thymol, carvacrol and cymol. Commercial grades are N.F., and technical red and white.

Savory oil is the essential oil distilled from summer savory, *Satureia hortensis,* and is used in flavors and occasionally in perfumes.

Parsley oil is a colorless to yellow viscous liquid expressed from the seed of *Carum petrolelenum.* It consists largely of **apiol** or **parsley camphor,** 1-allyl-2,5-dimethoxy-3,4-methylenedioxybenzene, $C_3H_5(CH_3O)_2C_6H:O_2:CH_2$. This ether is characteristic of the oil. Parsley oil is used in odorants and flavors. It is sometimes considered as an oleoresin.

Sassafras oil is distilled from the bark of *Sassafras officinalis.* It contains about 80 per cent of safrol, 7 of camphor, 0.5 of eugenol and 10 per cent of pinene and phellandrene. There is a U.S.P. grade. The yellow to reddish oil is used in flavoring, medicine and perfumery. An **artificial sassafras oil** is also available.

Valerian oil is distilled from the roots and root-like stems of the common valerian plant, *Valeriana officinalis.* **European valerian oil** contains borneol, pinene, camphene, esters of borneol and valerianic acid. **Japanese valerian oil** cannot be readily distinguished from the European variety. It is used in perfumes and as an industrial odorant.

Bitter almond oil is not to be confused with sweet almond oil, the former being an essential oil from *Amygdalus communis,* the latter a nondrying oil from dried ripe bitter almonds or other kernels containing amygdalin. It is freed from fixed oil by maceration with water and steam distillation. Bitter almond oil is a colorless to yellow refractive liquid, with an odor of **benzaldehyde,** which is the main constituent. The oil is optically inactive or slightly dextrorotatory. U.S.P. oil contains not less than 95 per cent of benzaldehyde and not less than 2 per cent nor more than 4 per cent of hydrogen cyanide. Only oil free from hydrogen cyanide is suitable for use as a flavoring agent. Aside from medicinal purposes it is used in cosmetics, and the cyanide-free grade as a flavor in foodstuffs and liqueurs. The cyanide-free oil is known as bitter almond oil S.A.P. This symbol for *sans aciduum prussicum* means without prussic or hydrocyanic acid. Essential oils from peach kernels and apricot kernels are so similar that they are used as adulterants. **Artificial bitter almond oil** is benzaldehyde.

Peach kernel oil is distilled with steam from peach kernels from *Amygdalus persica,* the fatty glycerides having first been removed by expression. It is similar to, and used as a substitute for oil of bitter almonds.

Lemongrass oil or **Indian verbena oil** is obtained by the distillation of an East Indian grass, *Cymbopogon citratus.* The yellow to brown oil has a fragrant odor and contains citral, geraniol and methyl heptanone. The native oil is sold for use in perfumery and in various industrial products as an inexpensive odorant. A more expensive rectified grade is also sold for similar purposes.

Verbena oil is steam-distilled from the leaves of *Lippia citridora* or related species. The yellow oil used in perfumes is not to be confused with Indian verbena oil which is lemongrass oil.

Vetiver oil is distilled from the roots of the East Indian grass, *Vetiveria zizanioides,* cultivated in the tropics and in Louisiana. **Java vetiver oil** contains citral, limonene and geraniol; **Réunion vetiver oil** or **Bourbon vetiver oil** contains a sesquiterpene, a sesquiterpene alcohol and palmitic and benzoic acids. It is used as a perfume oil and is sometimes called **vetivert oil** or **rhuskhus oil.**

Cypress oil is distilled from the fresh leaves and young shoots of the cypress tree, *Cupressus sempervirens.* Among its main constituents are furfurol, pinene, camphene, terpineol, cypress camphor and cadinene. Imported grades sell at more than double the price of the domestic oil. The pale yellow liquid is used in medicine, largely as an inhalant.

Cinnamon oil or **cinnamon-leaf oil** is obtained by distilling the leaves of *Cinnamomum zeylanicum.* The oil contains 65-95 per cent of eugenol, cinnamic aldehyde, safrol, terpenes and benzaldehyde. The pale yellow oil has an odor of cinnamon and cloves and is used in medicine, flavoring and perfumery. **Seychelle cinnamon oil** has a higher specific gravity but is similar to **Ceylon cinnamon oil** in color, odor, and application.

The Seychelle oil is much less expensive. The U.S.P. grade contains not less than 80 per cent by volume of cinnamic aldehyde. True **cinnamon-bark oil** is relatively rare, and very expensive.

Cassia oil is obtained by distilling the twigs and leaves of shrubs or trees known as *Cinnamomum cassia* and is sometimes known as **Chinese cinnamon oil.** The yellow to brown oil has a cinnamon-like odor, which is not as fine as that of cinnamon, and a very sweet taste. It contains 65-70 per cent of cinnamic aldehyde. It is much less expensive than cinnamon oil and should not be confused with the latter, although they are classed as the same in the U.S. Pharmacopoeia. A redistilled grade is used in flavoring and in perfumery.

Pepper oil is ordinarily **oil of black pepper,** the colorless to yellow or greenish volatile oil steam-distilled from the unripe fruit of *Piper nigrum.* It is high in phellandrene and is used medicinally.

Bay oil or **bayleaf oil** is obtained by distillation from the leaves of the West Indian bayberry tree, *Pimenta acris.* It contains eugenol, chavicol and myrcene. The yellow oil is used in perfumes, particularly in bay rum. A terpeneless grade is also sold which is of about double strength.

Expressed laurel oil is an ether-soluble solid obtained from the fresh fruit of *Laurus nobilis.* It consists of the triglyceride of lauric acid with volatile oil and is a natural fat known as bayberry wax, rather than a true essential oil. **Distilled laurel oil** is also known as **oil of sweet bay.** It is distilled from the leaves of the same shrub and is not to be confused with oil of bay from a variety of pimento. The oil is soluble in alcohol, chloroform or ether and contains pinene, eugenol, and cineol. It is used as an odorant.

Myrtle oil is the yellow to greenish distillate from the leaves of *Myrtus communis.* It contains pinene, eucalyptol, camphor, dipentene, etc. and is used medicinally for antiseptic and astringent properties.

Caraway oil or **caraway-seed oil** is obtained by the distillation of caraway seeds from *Carum carvi.* The caraway plant is cultivated in various parts of the world including the United

States. The oil contains eugenol, phenol, carvone and *d*-limonene. A Dutch grade is sometimes quoted. The colorless oil is sold in a U.S.P. X grade soluble in 8 volumes of 80 per cent alcohol, for use in medicine, liqueurs and flavors. The oil is also used in compounding soap perfume.

Clove oil is obtained from the flower buds of an East Indian tree, *Eugenia aromatica*. The yellow oil has a pungent, spicy odor and taste. It contains over 80 per cent of eugenol and some caryophyllene. The U.S.P. grade contains a minimum of 82 per cent by volume of eugenol. It is used in medicine, flavoring and perfumery.

Mustard oil or **mustardseed oil** is obtained by expressing the seeds of the black mustard plant, *Brassica nigra*. The colorless to yellow oil becomes brown on exposure to light. It contains over 90 per cent of allyl isothiocyanate. Natural, expressed, and artificial U.S.P. grades are sold for use in medicine. The U.S.P. grade must contain not less than 93 per cent of allyl isothiocyanate. **Artificial mustard oil** is allyl isothiocyanate, C_3H_5CNS, obtained from natural mustard oil or by the distillation of allyl iodide with an alcoholic solution of potassium thiocyanate.

Pimento oil or **allspice oil** is distilled from the berry of the allspice tree, *Pimenta officinalis*. The yellow to brown oil has an odor resembling that of cloves. It contains eugenol and sesquiterpenes. A somewhat similar oil is obtained from the leaf of the same tree. Both **pimento-berry oil** and **pimento-leaf oil** are quoted, the latter being much less expensive. These oils are used in medicine and in flavoring products.

Spearmint oil is distilled from the leaves of the common garden mint, *Mentha spicata*. The oil is colorless to pale yellow. It contains carvone, limonene and pinene. The U.S.P. grade yields not less than 50 per cent by volume of carvone, and is sold for flavoring. A terpeneless grade offered is double strength.

Sweet basil oil or basil oil is a yellowish oil distilled from the leaves of the sweet basil, *Ocinum basilicum*, a species of mountain mint. The oil from Réunion is sometimes distinguished from the ordinary oil. Ingredients are camphor, pinene, cineol, linalool, etc. It is extremely soluble in alcohol and used in flavors, perfumes and medicines.

Calamus oil is distilled from the rhizomes of sweet flag, *Acorus calamus*. The yellow to brown oil has a saponification value of 6-20. It contains asarone and eugenol, and acetic, oenanthilic, heptylic and palmitic acids. This oil is used in medicine and in making perfumes and liqueurs.

Tansy oil is distilled from the tansy herb, *Tanacetum vulgare*. It contains thujone, camphor and borneol. The yellow liquid becomes brown on exposure to air and is used in medicine.

Garlic oil is the volatile yellow oil steam-distilled from the bulb or clove or the entire plant of *Allium sativum*. It is high in complex sulfides. The objectional odor in concentrated form becomes a pleasant odor or flavor in small amounts. It is very expensive, and used medically and as a flavoring material.

Wormwood oil is distilled from the leaves of a European woody herb, *Artemisia absinthium*. It contains thujone, its acetate, and the alcohol phellandrene, as well as cadiene and palmitic acid. The green to brown oil is used in medicine.

Pennyroyal oil comes from two sources, European and domestic. **European pennyroyal oil** is distilled from the plant *Mentha pulegium*, **American pennyroyal oil** from the leaves and tops of *Hedeoma pulegioides*. Both oils are yellow, although the European oil may be more reddish and show a blue or green fluorescence. Both oils have a mint-like odor, and contain pulegone. The American oil also contains other ketones and free fatty acids; the European also menthol and menthone. The domestic is but slightly cheaper than the imported grade. They are used in medicine and as an insect repellent.

Wintergreen oil, wintergreen-leaf oil or **Gaultheria oil,** is distilled from the leaves of the evergreen herb, *Gaultheria procumbens*. The colorless to yellow or red oil is sold as northern and southern. The latter is less expensive. It contains 96-99 per cent of methyl salicylate, the U.S.P. grade not less than 98 per cent. It is used in medicine, as an odorant, and for flavoring. **Synthetic wintergreen oil** is the ester, methyl salicylate.

Bergamot oil is expressed from the rind of a pear-shaped fruit, *Citrus aurantium,* which is grown in southern Italy and Sicily. Its odor is due to the presence of linalyl acetate and related compounds. A terpeneless grade is also available and is over twice as strong as the usual quality. The natural oil has been largely adulterated because of its high cost. **Artificial bergamot oil** is much less expensive and has much the same odor as the natural oil because of its content of linalyl acetate. The oil is used in perfumery, particularly in soap perfumes, in hair oils and pomades, and in disinfectant products.

Betula oil, birch oil or **sweet-birch oil** is obtained by distillation of the bark and twigs of many varieties of *Betula* birch trees. The yellow to colorless oil resembles oil of wintergreen in odor and taste, since methyl salicylate is the chief constituent. It is grouped with synthetic methyl salicylate and natural oil of wintergreen by the U. S. Pharmacopoeia. Grades are northern and southern, rectified and crude. The southern grades are much less expensive. It is used like oil of wintergreen in flavoring products and as an odorant.

Orris oil is a semisolid fatty volatile oil obtained from the rhizomes of *Tris florentina* or white flag, a European plant. It contains fatty acids and their esters, with irone and unknown odorous materials, and is soluble in alcohol, ether or chloroform. The quoted grade is as a Florentine concrete at several dollars per ounce, which makes it nearly as expensive as a liquid oil. It is used in perfumes and cosmetics.

Rue oil is the volatile oil from *Ruta graveolens,* a yellowish to greenish liquid, often fluorescent. It contains at least 90 per cent of methylnonyl ketone with some of the heptyl compound. It comes from France, Spain, Syria and Northern Africa, and is very soluble in alcohol. Medically it is an irritant, anthelmintic, rubefacient, antiepileptic, antispasmodic and emmenagogue, particularly in veterinary medicine.

Petitgrain oil is distilled from the leaves, twigs and unripe fruit of the bitter orange tree, *Citrus bigaradia.* Among its constituents are linalyl acetate, linalool, dipentene, pinene, pyrrol, furfural, terpineol, nerol and geraniol. Grades sold include Algerian, French and South American, the French being most expensive. A terpeneless grade is about triple strength. It is used in odorants.

Neroli oil is distilled from the fresh flowers of the bitter orange, *Citrus aurantium.* It contains linalyl acetate, linalool, geraniol, methyl anthranilate, pinene, camphene, dipentene, terpineol, nerol and paraffins. The yellowish fluorescent oil turns brown on exposure to light. It has a pleasant, orange-blossom odor and a bitter taste, and is used in perfumery and flavoring. It is very expensive. Special grades obtained by enfluerage are also available. **Artificial neroli oil** is sold at a much lower price.

Lavender oil or **lavender-flower oil** is distilled with steam from several varieties of lavender blossoms. The yellow to green oil has the well-known lavender odor and is used widely in perfumery. The usual oil is from French flowers, and contains 30 to 40 per cent of linalyl acetate and lesser amounts of linalool, fatty acid esters, geraniol and coumarin. **English lavender oil** contains a smaller quantity of esters than **French lavender oil** and more of other ingredients, so that the odor is different. The English oil is the more expensive. Quotations are on the basis of ester content such as U.S.P. 50 per cent, U.S.P. 38-42 per cent, U.S.P. XI 35 per cent, U.S.P. XI 30 per cent, U.S.P. IX 30 per cent and U.S.P. VIII 30 per cent, prices varying accordingly. U.S.P. XI lavender oil containing a minimum of 30 per cent of esters calculated as linalyl acetate, is the official grade. Terpeneless lavender oil is about double strength. Another grade sold as garden lavender oil is conventionally an inexpensive imitation. **Lavender-spike oil or aspic oil** is distilled from the flowering herb *Lavandula spica,* and contains camphor, borneol and camphene. A spanish grade is quoted. The yellow oil has an odor which appears to combine that of lavender and rosemary. A technical grade is sold. Lavender-spike oil is used in veterinary medicine.

Lavendin oil is a perfume oil with an odor resembling lavender and camphor. It is distilled from the flowers of a European plant, *Lavandula latifolia fragrens,* a cross of lavender and spike.

Chamomile oil or **camomile oil** is distilled from the flowers of the chamomile, the german oil being from *Matricaria chamomilla* and the Roman oil from *Anthemis nobilis.* The liquid is blue when freshly distilled but becomes brown on exposure to light. It is high in esters, and is used medically and as an odorant.

Tuberose oil is a colorless to very light colored oil obtained from the common garden flower, *Polianthes tuberosa,* by enfleurage. It is an expensive perfume oil.

Jasmine oil is colorless to light yellow, and obtained from *Jasminum officinale* or *Jasminum grandiflorum* by enfleurage. It is high in benzyl acetate, linalyl acetate, linalool and indol, and is an expensive perfume oil.

Violet oil is a colorless to very light yellow oil derived from the violet, such as *Viola cucullata,* by enfleurage. It is very expensive, and is used in perfumes.

Jonquil oil or **narcissus oil** is the colorless or very light oil from the flowers of *Narcissus jonquilla.* It is very expensive and is used in perfumes.

Mimosa oil is a colorless to light yellow oil from the flowers of the genus of shrubs known as mimosa. It is expensive and used as a perfume oil.

Oak-moss oil is distilled from oak-moss resin. The light yellow and decolorized grades find a place in perfumes to replace the resin.

Cedarwood oil is obtained by distillation of many varieties of cedar wood and is also collected as a by-product during the manufacture of lead pencils. The oil from the original distillation has a higher specific gravity than the by-product oil. Southern and Oregon oils are sold. The colorless to greenish-yellow oil, containing cedrene and cedar camphor, is used in medicine, in perfumery, as an insect repellent, and as an industrial odorant.

True **cedarleaf oil** is obtained by distilling the leaves of the cedar tree, although the leaves of other conifers may often be mixed in for commercial production of the oil. Among the principal constituents are limonene, cadinene, borneol and bornyl esters, and pinene. The colorless oil is used in medicine and as an odor in commercial products such as polishes.

Pine-needle oil is obtained by the distillation of pine needles from the Scotch fir, *Pinus sylvestris* or *Pinus montana.* That from the latter is U.S.P., and known as **Oil of Pinus pumulionis,** the other being known as **Oil of Pinus sylvestris.** The chief constituents are bornyl acetate, limonene, pinene, dipentene, sylvestrene and various sesquiterpenes. The U.S.P. grade yields not less than 5 per cent of esters calculated as bornyl acetate. A Siberian grade is sometimes quoted. The colorless to pale yellow oil has an odor of balsam, and is used in medicine and in perfumery.

Turpentine or **turpentine oil** is an essential oil obtained by distillation of the oleoresin called crude turpentine, obtained as an exudate from numerous varieties of pine trees, or by steam distillation or destructive distillation of the stumps, waste wood and small branches of such trees. The latter is called **wood turpentine** to distinguish it from the former or **gum turpentine.** Gum turpentine is considered superior in quality to wood turpentine and commands a price premium. The colorless to yellow liquid consists mostly of pinene and has a marked odor. Turpentine dissolves rubber, sulfur, phosphorus and resins. Grades sold are gum turpentine—and steam-distilled and destructively distilled wood turpentine. The oil is used in paints, varnishes, lacquers, as a solvent, and in medicine. In addition to U.S.P. oil of turpentine, **rectified oil of turpentine** is a U.S.P. grade distilled from an aqueous sodium-hydroxide solution for internal use.

Sulfurated oil of turpentine, Haarlem oil, or **Dutch oil** is prepared by mixing one part of sulfurated linseed oil with three parts of oil of turpentine. The brownish red oil is sold in both imported and domestic grades. It is used as an antiseptic.

Olibanum oil is a fragrant yellow oil distilled from gum olibanum. It is also known as **oil of frankincense** and is used as an odorant.

Spruce oil is distilled from the needles and twigs of various varieties of the spruce tree. It contains pinene, cadinene and bornyl acetate. The colorless oil is used in medicine. **Hemlock**

oil is similarly distilled from the needles and twigs of the hemlock tree and contains pinene, bornyl acetate and sesquiterpenes. The colorless oil has a pleasant odor resembling balsam and is used in medicine.

Hop oil is distilled from the strobiles of the *Humulus lupulus.* The yellow to green or brown liquid is high in terpenes and geraniol. It has a powerful odor and is used medicinally and as a flavor, particularly for tobacco.

Cascarilla oil is the yellow to green distilled oil from the bark of *Croton elutria.* It contains largely terpenes and is extremely expensive. The faintly aromatic material has both medical and flavor uses.

Copaiba oil is the inexpensive, colorless to light yellow oil distilled from *Balsam copaiba.* The mixture consists largely of complex terpenes and is used in medicine.

Hyssop oil is the colorless to light yellow oil distilled from the herb, *Hyssopus officinalis.* It is expensive and used medicinally and as a flavor for liqueurs.

Marjorum oil is the yellow to yellow-green oil distilled from the marjorum herb, *Origanum marjorana.* It contains large amounts of terpenes, particularly terpinene. This oil is used medically in tonics and industrially in perfumes. It is not to be confused with oil of origanum, which is oil of thyme.

Rosemary oil is distilled from the fresh flowering tops of a shrub of southern Europe and Asia Minor, *Rosemarinus officinalis.* It contains pinene, camphene, cineol, camphor, borneol and its esters, and sesquiterpenes. The colorless to pale yellow oil is sold in U.S.P. and technical grades of Spanish oil for use in perfumery and medicine. The U.S.P. grade yields not less than 2.5 per cent of esters calculated as bornyl acetate, and not less than 10 per cent of total borneol, free and as esters. **Artificial oil of rosemary** is also available, as well as a terpeneless grade of triple strength.

Camphor oil is obtained by distilling the wood of the camphor tree, *Cinnamomum camphora,* and separating the oil from the solid camphor. The composition of the oil is highly variable since it is a by-product in the production of camphor. It may contain pinene, camphor, cineol, phellandrene, dipentene, safrol and eugenol. **White camphor oil** is a grade containing the lowest boiling portions, used as a turpentine substitute. **Sassafrassy camphor oil** contains safrol which gives it an odor resembling that of sassafras. It is used as a perfume in such products as soap, polishes and pharmaceutical preparations. Camphor oil is also used in medicine and for the manufacture of safrol.

Juniper-berry oil is distilled with steam from the dried berries of the Juniper tree, *Juniperus communis.* The colorless to yellow oil has a bitter taste and may tend to a turpentine-like odor. It darkens on exposure to air, and contains pinene, cadinene and camphene. It is a U.S.P. product soluble in 4 volumes of alcohol. A twice rectified grade is also sold. Oil of juniper is used in medicine and in the preparation of liqueurs. If used in flavoring gin in the United States, the product must be labeled as artificial gin. Terpeneless juniper oil is available of about double strength.

Juniper-wood oil is apt to consist of a mixture of juniper-berry oil and turpentine oil or of turpentine oil distilled over juniper wood, rather than of the pure distilled oil obtained from juniper wood and twigs. The usual composition is therefore variable. A technical grade is sold for use in veterinary medicine.

Cade oil or **juniper-tar oil** is obtained by destructive distillation of the wood of the European juniper tree. It contains cadinene and pinene. The thick brown oil is sold of U.S.P. grade for use in antiseptic ointments and in animal soaps, and has a specific gravity of 0.950-1.055 at 25°.

Cubeb oil is distilled from the nearly full-grown fruit of *Piper cubeba.* It contains cadinene, dipentene and sesquiterpenes. The colorless oil is sold as U.S.P. IX, soluble in 18 parts of 90 per cent alcohol and miscible with absolute alcohol, and is used in medicine.

Nutmeg oil or **myristica oil** is distilled from nutmegs, the seed of a tree, *Myristica fragrens*, cultivated in the East and West Indies, and in Brazil. The colorless to yellow oil has a strong nutmeg odor and spicy taste. It contains myristicin, pinene, borneol, terpineol, geraniol, safrol and several fatty acids and phenols. The U.S.P. grade is sold for flavoring and for use in medicine.

Mace oil is distilled from mace, the coating of nutmeg seeds. The pale yellow oil has an agreeable odor resembling that of oil of nutmeg. It contains pinene, dipentene, myristicol and myristicin. Distilled mace oil is used in flavoring and in perfumery.

Cognac oil consists largely of ethyl oenanthate or oenanthic ether. It is an oily liquid derived from the fermentation of grapes. The crude grade is green but when rectified it is colorless to light yellow. An artificial grade is also offered, probably of distinctly different constitution. The better grades have a pleasant wine odor and are used in flavors and odorants.

Cardamomseed oil is obtained from the seeds of an East Indian herb, *Eleteria cardamomum.* This expensive oil varies in its characteristics according to the locality from which it comes. The Malabar oil has a higher specific gravity than that from Ceylon but about the same refractive index. **Ceylon cardamomseed oil** contains terpinene, dipentene, acetic esters and limonene. **Malabar cardamomseed oil** contains cineol, borneol, terpineol and limonene. The pale yellow oil is used in medicine and in making liqueurs.

Cumin oil is distilled from the fruit of a dwarf plant, *Cuminum cyminum,* native to Egypt and Syria. It contains cymene and cumic aldehyde. The oil is used medicinally, and has much in common with oil of caraway.

Erigeron or **fleabane oil** is distilled from the flowering herb *Erigeron canadense.* The pale yellow oil darkens on exposure to the atmosphere and contains *d*-limonene, terpineol and esters. It is used as a medicinal, largely for antiseptic purposes.

Lemon oil is obtained by cold pressing fresh lemon peel. The pale yellow oil has a fragrant lemon-like odor and a somewhat bitter taste. It contains *d*-limonene and citral. U.S.P. lemon oil is obtained from the fresh peel of the fruit of *Citrus medica,* with or without the previous separation of the pulp and the peel, and is soluble in 3 volumes of alcohol. California and Italian grades are quoted. Terpeneless lemon oil is about 14-times strength.

Lime oil is obtained by distillation or by expression of the peel of the West Indian lime, *Citrus aurantifolia.* The distilled oil has an unpleasant odor of turpentine and contains *d*-limonene and terpinene. The more expensive expressed oil is golden-yellow in color, has an intense odor resembling that of lemon oil, and contains *d*-limonene, citral and methyl anthranilate. Both are used to some extent in perfumery and in flavoring. Imitation lime oil is also sold, as well as terpeneless lime oil of about 16-times strength.

Grapefruit oil is obtained from the expression of fresh grapefruit rind, usually from *Citrus maxima.* The pale yellow oil has a citrus type of odor and is used mainly in flavors. Terpeneless oil of about 30-times normal strength is also available.

Sweet orange oil may be distilled oil but is usually obtained by cold pressing from the peelings of sweet oranges, *Citrus aurantium.* It contains at least 90 per cent of *d*-limonene, with terpenes. The yellow to deep orange or brown oil has an orange odor and a mild taste. The U.S.P. grade is expressed. The less expensive, distilled oil is sold, as well as the expressed oil. The latter is offered according to the origin, as from Africa, California, Florida, Messina, and the West Indies. The oil is used in flavoring, perfumery and medicine. A terpeneless grade about 35-times strength is available.

Mandarin oil is the yellow oil expressed from the fresh peel of the mandarin orange, *Citrus nobilis*, grown in semitropical regions. It contains esters of anthranilic and methylanthranilic acids with limonene. It is moderately soluble in alcohol and used as a flavoring ingredient. It is much more expensive than orange oils.

Celeryseed oil is obtained by the distillation of celery seeds from *Cipium graveolens.* It contains limonene, phenols, sedanolide, sedanonic acid and palmitic acid. The greenish yellow oil has the taste of celery and is used in flavoring and in medicine.

Dillseed oil is obtained by distilling the fruit of the herb *Anethum graveolens.* The pale yellow oil has a penetrating odor and a sweetish taste which becomes sharp. It contains phellandrene, carvone and limonene. Dutch and East Indian grades are quoted for use in flavoring and in perfumery. The oil is also produced from the weed itself as **dill-weed oil.**

Angelica-root oil is an expensive oil obtained from the roots of herbs of the angelica family, by steam distillation. It contains phellandrene and valeric acid. The colorless oil becomes yellow on exposure to the atmosphere. It has a spicy taste and is used in liqueurs and in medicine.

Angelica-seed oil is obtained by steam distillation from the seeds of the herb, angelica, and is even more expensive than the root oil. The oil becomes yellow on standing. It contains phellandrene and valeric acid, is of better quality than the root oil, and is also used in liqueurs and in medicine.

Ginger oil is distilled from the root-like stem of the plant *Zingiber officinale.* It contains phellandrene, *l*-zingiberene, *d*-camphene, cineol, citral and borneol. The pale yellow oil has a somewhat burning taste. It is used in flavoring and in making liqueurs.

Capsicum oleoresin is obtained from the fruit of the tropical pepper plant, *Capsicum fructescens.* It contains fixed oils, capsaicin, capsicin and capsicol. The U.S.P. VIII grade is sold for use in medicine and flavoring.

Guaiac-wood oil or **champaca-wood oil** is a viscous oil with an odor resembling that of tea or violets. It is obtained in the form of a concrete from varieties of *Guaiacum* grown in South America, and is used in perfumes.

CONSTANTS FOR ESSENTIAL OILS

Oil	Specific Gravity at 15° C.	Refractive Index at 20° C.
Linoloe-wood	0.870-0.891	1.460-1.466
Coriander-seed	0.870-0.888	1.463-1.471
Ylang ylang, Manila	0.930-0.947	1.491-1.500
Ylang ylang, Cananga	0.908-0.967	1.480-1.508
Snakeroot, Canada	0.951-0.952	
Origanum	0.898-0.960	1.495-1.523
Patchouli	0.966-0.995	1.507-1.513
Lovage	1.000-1.040	
Ambrette-seed	0.905-0.917	1.474-1.480
Sandalwood, East Indian	0.973-0.985	1.504-1.509

CONSTANTS FOR ESSENTIAL OILS—*Continued*

Oil	Specific Gravity at 15° C.	Refractive Index at 20° C.
Sandalwood, West Indian	0.950-0.970	1.508-1.513
Sandalwood, Australian	0.970-0.973	1.504-1.507
Wormseed, American	0.963-0.990	1.474-1.484
Wormseed, Levant	0.930-0.935	1.465-1.469
Anise	0.980-0.990	1.544-1.560
Tarragon	0.890-0.960	1.516-1.517 (15°)
Sage	0.915-0.925	
Fennel-seed	0.965-0.977	1.528-1.539
Peppermint	0.896-0.921	1.460-1.468
Citronella	0.885-0.901	1.463-1.475
Geranium	0.888-0.907	1.460-1.473
Rose	0.823-0.880	1.460-1.464
Palmarosa	0.887-0.900	1.472-1.477
Cajeput	0.917-0.930	1.466-1.472
Eucalyptus	0.867-0.927	1.449-1.496
Savin	0.907-0.930	1.473-1.480
Thyme, French or German	0.905-0.915	1.480-1.493
Thyme, wild	0.873-0.920	
Parsley	0.900-0.925	c. 1.489
Sassafras	1.070-1.080	c. 1.530
Valerian, European	0.920-0.965	c. 1.486
Valerian, Japanese	0.960-1.004	1.477-1.487
Almond, bitter	1.045-1.070	1.532-1.544
Lemongrass	0.870-0.912	1.482-1.489
Verbena	c. 0.900	
Vetiver, Java	0.993-1.044	1.519-1.531
Vetiver, Réunion	0.990-1.020	1.515-1.529
Cypress, French or Algerian	0.868-0.884	1.470-1.476
Cypress, German	0.880-0.900	1.474-1.480
Cinnamon	1.044-1.065	1.531-1.540
Cassia	1.055-1.070	1.600-1.606
Pepper	0.870-0.930	
Bay	0.960-0.985	1.506-1.520
Laurel-berry, expressed	0.915-0.935	
Laurel-leaf, distilled	0.920-0.930	
Myrtle	0.890-0.920	
Caraway	0.907-0.919	1.484-1.488
Clove	1.043-1.068	1.529-1.537
Mustard	1.014-1.022	1.527-1.529
Pimento	1.018-1.048	1.525-1.536
Spearmint	0.920-0.940	1.482-1.492
Sweet basil, European	0.905-0.930	
Sweet basil, Réunion	0.945-0.987	
Calamus	0.959-0.972	1.503-1.510
Tansy	0.925-0.935	1.457-1.462
Garlic	1.046-1.057	
Wormwood	0.901-0.954	1.460-1.474
Pennyroyal	0.925-0.950	1.482-1.488
Wintergreen, natural	1.180-1.193	1.535-1.536

CONSTANTS FOR ESSENTIAL OILS—*Continued*

Oil	Specific Gravity at 15° C.	Refractive Index at 20° C.
Wintergreen, synthetic	1.180-1.185	1.497-1.538
Bergamot	0.881-0.886	1.465-1.471
Betula	1.180-1.189	1.536-1.538
Orris	0.930-0.940	c. 1.495
Rue	0.833-0.842	c. 1.434
Petitgrain	0.885-0.900	1.459-1.466
Neroli	0.870-0.881	1.468-1.474
Lavender-flower	0.880-0.904	1.458-1.476
Lavender-spike	0.900-0.922	1.464-1.468
Chamomile	0.905-0.915	c. 1.445
Tuberose	1.007-1.035	
Jasmine	1.007-1.018	
Cedarwood	0.943-0.964	1.500-1.510
Cedarleaf	0.887-0.900	c. 1.468
Pine-needle	0.860-0.925	1.469-1.480
Turpentine	0.858-0.877	1.471-1.474
Olibanum	0.875-0.885	
Spruce	0.900-0.930	1.472-1.480
Hemlock	0.900-0.930	1.472-1.480
Hop	0.840-0.882	c. 1.477
Cascarilla	0.900-0.925	1.491-1.496
Copaiba	0.895-0.905 (25°)	
Hyssop	c. 0.932	
Marjorum	0.890-0.910	
Rosemary	0.894-0.920	1.466-1.473
Camphor	0.870-1.040	
Juniper-berry	0.860-0.882	1.472-1.484
Juniper-wood	c. 0.869	c. 1.471
Cade	0.980-1.055 (25°)	1.468-1.504
Cubeb	0.915-0.930	1.494-1.498
Nutmeg	0.865-0.925	1.479-1.488
Mace	0.910-0.930	1.479-1.488
Cognac	0.875-0.885	
Cardamomseed, Ceylon	0.895-0.906	1.460-1.470
Cardamomseed, Malabar	0.923-0.941	1.462-1.467
Cumin	0.900-0.930	1.494-1.507
Erigeron	0.857-0.868	c. 1.490
Lemon, California	0.853-0.861	1.473-1.475
Lime, distilled	0.860-0.870	1.470-1.471
Lime, expressed	0.878-0.901	1.482-1.486
Orange, sweet	0.847-0.859	1.470-1.475
Mandarin	0.850-0.858	
Celery-seed	0.866-0.898	1.478-1.486
Dillseed	0.895-0.915	1.480-1.495
Angelica-root	0.857-0.918	1.476-1.488
Angelica-seed	0.856-0.890	1.484-1.491
Ginger	0.877-0.886	1.489-1.494
Guaiac-wood	0.965-0.975 (30°)	

CHAPTER XXXIV

NATURAL GUMS, RESINS AND BALSAMS

Gums, resins, and balsams form a complex group of non-crystalline substances. Some of the balsams are called oleoresins but are unlike those described with essential oils in another chapter. Since they are derived from natural vegetable, or occasionally animal sources they overlap, the majority of them being mixtures of substances in more than one class. The term gum is applied to many of them but not all. For the meaning of medical terms given under uses, refer to Appendix B.

Water-soluble gums are largely the dried saps of vegetation. They either swell to a jelly in water to form mucilaginous semiliquids, disperse to form colloidal systems, or dissolve in water. While organic, more or less combined magnesium, calcium and potassium may be present. In general the gums are largely carbohydrates. Some are glucosides formed by combination of an organic acid with sugars. In connection with natural gums also see Irish moss, carob seed, agar agar, quince seed, locust kernel, locust bean, gelatin, and pectin in other chapters, as they have similar properties.

Natural resins are also largely exudates from trees or plants, but are not water-soluble. Shellac is an exception, an excretion of an insect. Some dissolve in alcohol to form **spirit varnish,** others by heating become soluble in linseed oil, giving compositions which, cut with turpentine and petroleum solvents, are **resin varnishes.** In the latter case the resins are called **varnish resins.** Some are obtained from trees and are called **gum resins.** Others are found buried in the earth, from past ages. The latter are known as **fossil resins. Oleoresins** are mixtures of volatile oils and resins, and have been classed with the volatile or essential oils to which they are related. Lest the problem seem simple, natural resins may be mixtures of water-soluble gums and resins. The substances which because of elasticity have the properties of chewing gum, fall in this class. A **balsam** is ordinarily a liquid or a soft solid and consists of resin and volatile oils, often associated with vanillin, benzoic acid, etc. But this class, too, is merely a shading off from other classes.

Gum tragacanth is a hard and brittle gum obtained as an exudate from various species of *Astragalus* tree growing in eastern Europe and Asia. Starch grains are present. Hydrolysis produces arabinose, galactose, geddic acid and an insoluble portion, bassorin. Gum tragacanth swells in water rather than dissolving, a thick dispersion being produced with less than one per cent of the high-quality material. A clear solution is not obtainable. Commercial grades are yellow to white in color and are sold by number from 1 to 6. The gum is also sold as Turkish or Aleppo. There is a U.S.P. grade meeting specific tests for quality. Flake and dust are sold but the best grades of tragacanth are in ribbon form. In general, finely ground tragacanth rarely gives as good dispersions as are obtained with the ribbon grades. Gum tragacanth is very generally used as a thickener for aqueous liquids and is permissible in food products. Products in which it is used range from calico-printing fluids to flavoring substances, from leather dressings to adhesives, from hair-waving liquids to soups. U.S.P. **tragacanth mucilage** contains 6 grams of gum tragacanth and 18 grams of glycerine per 100 grams of aqueous mixture.

Gum karaya or **Indian gum** is obtained from *Sterculia campunulata* and several other East Indian trees. It is best described as a low grade of gum tragacanth and tends to be highly colored. Grades are XXX, XX, and numbers 1 and 2. It is used as a substitute for gum tragacanth and displaces it wherever possible, since its cost is about one-tenth that of tragacanth.

Gum arabic or **gum acacia** is the gummy exudate obtained from *Acacia senegal, Acacia arabica* and other species of acacia. These grow throughout the tropics and belong to the mimosa family. The gum is produced in various parts of the world and varies from yellow to white according to quality. It is one of the most important products of the Sudan, being only exceeded in volume of production by cotton. Gum arabic is composed essentially of the calcium salt of arabic acid, and on hydrolysis yields arabinose, galactose and arabinosic acid. Grades sold are amber sorts, cleaned, white sorts, numbers 1 and 2, and powdered. The gum is used as an emulsifying agent, in pharmaceuticals, adhesives, ink, in the printing of textiles and for many miscellaneous purposes. U.S.P. gum acacia yields not more than 1 per cent of water-insoluble residue, not more than 4 per cent of total ash, not more than 0.5 per cent of acid-insoluble ash, and not more than 15 per cent of moisture. U.S.P. **acacia mucilage** contains 35 grams of acacia and 0.1 gram of sodium benzoate per 100 cc. of aqueous mixture. It is a common excipient for pharmaceutical tablets.

Gum senegal is a variety of gum arabic obtained from the vicinity of Senegal in French West Africa. Grades sold are picked and sorts, at prices close to those of gum arabic. Uses are similar.

Gum ghatti is a low grade of gum arabic obtained from the *Dhava* and related trees of India and Ceylon. It is sometimes called **British Indian gum,** not to be confused with Indian gum or karaya. It occurs as yellowish tears. Soluble and superior grades are sold, the soluble being the more expensive. Its cost is less than half that of acacia and it is largely used to replace acacia.

Gum talha, talco gum, Suakin gum or **gum savakin** is a brittle variety of gum arabic obtained from the North African acacia trees, *Acacia stenocarpa* or *Acacia seyal.* It is lower in price and quality but used for purposes similar to those of gum acacia.

Gum copal is a general name applied to types of resins which may be hard or soft. In general the term is applied to soft nonfossil resins and excludes such types as kauri, but these are also sometimes called copals. The varied tropical habitats lead to confusion of names due to copals being sold under the name of the district in which gathered, or the seaport from which shipped. It is even said that resin from the same region may in part go through one port, in part through another, so that the same resin can become two different varieties of copal according to chance.

Congo copal is the broadest classification ranging from water-white transparent through 26 grades by number, to pale dust. Grades are by color and form, such as straw, amber, etc.; bold, nubs, sorts, fingers, chips, etc. Prices vary widely between the best, the usual average varieties and the cheapest. **Batu copal** comes from the Batu Islands of the Dutch East Indies and is of relatively low grade, bold scraped, bold unscraped, nubs, chips, and dust. It is related to damar. **Macassar copal** is from a port on the Island of Celebes in the Malay archipelago. It contains some fair grades, running from pale bold, nubs and chips to dust. **Singapore copal** is from that port at the tip of the Malay peninsula. It is similar to Macassar but of slightly lower grade. **Manila copal** is of complex classification including Philippine manila, Boeas, Loba, Şambas and spirit-soluble, in many lettered or descriptive grades. **Pontianak copal** is from a port in Borneo and is of relatively good quality as compared with other East Indian copals.

With the multitude of varieties, a statement that soft copals are soluble in ether or alcohol will have its exceptions, if to no greater extent than from the contaminants in many grades. Hard copals are soluble in linseed oil or turpentine after heating. As a matter of fact, copals differ from each other more than do many other individual gums of dissimilar name. It follows that description of a gum as a copal is merely a general statement unless more details are furnished as to type, grade, etc. Among the many uses of copals are for the manufacture of varnishes, lacquers, sizes, plastics, cements, etc.

Gum Yacca is a West Indian gum having the general properties of a copal and sold in lump or powdered forms.

Shellac is a resin obtained as an excrescence on the small twigs of several species of trees in the East Indies. It is produced as an excretion of an insect, *Coccus lacca,* which uses the twigs as a source of food. The constitution is complex. Natural shellac is purified by melting and pressing through crude bags of fabric. At least one plant purified by modern engineering methods. Orpiment, arsenic sulfide, is often added in crude refining as a pigment to improve the color. Grades of orange shellac vary upward from T.N. through superfine, a slightly better grade, to D.C., VSO, Diamond, etc., reaching nearly double the price of the cheapest grade. Garnet lac is a grade of unbleached shellac in particles resembling natural garnets.

Refined shellac has had the wax removed by dissolving the alcohol-soluble portion. While ordinary shellac is described as soluble in alcohol it gives an opalescent liquid rather than a clear, transparent solution, wax being suspended as a dispersed colloid. This is quoted at about double the price of the T.N. grade. **Bleached shellac** is produced by dissolving shellac in aqueous alkali and bleaching with sodium hypochlorite. It is then precipitated by neutralization. The product is sold on a bone-dry basis. Some grades become insoluble in alcohol due to reaction with oxygen from the air.

Shellac varnish is a solution of shellac in alcohol. It is graded by the number of pounds dissolved or cut in each gallon of alcohol. Thus white or orange shellacs are sold in 5-, 4½- or 4-pound cuts. Aside from its use in spirit varnish, shellac is used in its various grades in lacquers, plastics, insulating materials, phonograph records, sealing wax, ink, rubber compounds, as a grinding agent, as a stiffening agent in millinery and for many other purposes. On heating it gradually polymerizes to become insoluble.

Gum rosin or **colophony** is obtained as an exudate, mixed with a volatile oil, by the incision of coniferous trees. The volatile oil, turpentine, is distilled off, leaving the amorphous solid resin. Gum rosin is yellow to black and has a specific gravity of about 1.08 at 25°C. Its production is largely limited to the United States. Rosin is soluble in alcohol, ether, benzene, glacial acetic acid and many oils. It dissolves in aqueous alkalies by reaction to form soaps. Rosin consists of 80-90 per cent of abietic acid with 5-6 per cent of its anhydride and some other complex acids. There is a U.S.P. standard of acid value over 150 and ash not more than 0.05 per cent. Grades are based on color as established by government standards, the darkest being grade B, then varying through D, E, F, G, H, I, K, M, N, WG, WW to X. Sale is on the basis of quotations in barrels, which have a gross weight of 280 pounds, a net of about 235 pounds.

The darker products are used for making linoleum, rosin oil, and dark varnishes. The next series is used in making size for paper. Lighter grades are consumed in soap manufacture. The lightest grades are used for making light varnishes, adhesives, as a soldering flux, and in munitions. Rosin is also used to make resinates of lead, cobalt, etc. used as paint driers, in sealing wax, plastics, a synthetic resin in the form of the glyceryl ester called ester gum, and various other products. In general, varnishes containing much rosin are of inferior quality.

Wood rosin is similar in composition, properties and uses to gum rosin. It is obtained by extraction, steam-distillation or destructive distillation of the stumps and roots of long-leaf pine, left from lumbering. The wood rosin remains on distilling the turpentine from the first distillate. It has a higher specific gravity than gum rosin. Usual grades are FF, I, K, M, N, WG and WW. Because of uniformity of quality and dependability of supply, the price has become as high as that of gum rosin.

Gum kauri is a colorless to brown fossil resin found in the ground where the kauri tree, a New Zealand timber tree, has grown. It is sometimes known as a **hard copal resin** to distinguish from the soft copals. The resin is almost insoluble in solvents and oils except by heating with turpentine, linseed oil or petroleum spirits. Brown kauri is sold as XXX, BX and B1, B2 and B3, varying in price by 300 per cent. There is also an 80 per cent chip grade. Similarly, pale kauri is sold as XXX, 1, 2 and 3 with similar price variations. Gum kauri is used in many types of varnish and as a substitute for amber.

Amber or **gum amber** is the fossil resin from the extinct pines of the oligocene period. It is found in Scandinavia and on the shores of the Baltic Sea, and consists of oxidized resinous materials. Amber is yellow to red or brown, and may be semitransparent. It is used in the preparation of succinic acid, for distillation of oil of amber, and for pipe bits, ornaments, etc.

Gum dammar or **gum damar** is a yellowish white resin containing substantial amounts of wax, obtained from various evergreen trees of East India, the Philippines, Australia and New Zealand. It is soluble to give an opalescent solution in alcohol, ether, chloroform, carbon bisulfide and turpentine. The usual form is as roundish or irregular masses. It is semi-transparent and of varying hardness according to the amount of volatile oil present. **Batavia dammar** is sold in several grades by letter. **Singapore dammar** is sold as numbers 1, 2 and 3, chips, dust and seeds. The variation in price and quality from the high to the low grades is very great. For some purposes dammar is dissolved in solvents, filtered, and the solution evaporated to give **dewaxed dammar.** Gum dammar is used in making colorless varnish and lacquer, and related products. Dammar is applied to animal and vegetable specimens in the form of a solution for their preservation.

Dragon's blood is a resin which exudes to the surface of the fruit of the Malayan rattan palm or of other species of *Calamus.* The dark red amorphous solid is sold as a mass or in the form of thin reeds, and is odorless. It is soluble in alcohol, ether, chloroform and many types of oils. Dragon's blood is used as a pigment for coloring varnishes, paints, lacquers, dentrifrices, polishes, papers, plasters, stoneware, etc. and in photoengraving.

Gum guaiac or **resin guaiac** is a resin obtained from the wood of various varieties of *Guaiacum* trees growing in the West Indies and tropical America. It occurs as brown or greenish brown irregular lumps, soluble in alcohol, ether, acetone, chloroform and aqueous alkalies. This gum contains about 70 per cent of guaiaconic acid, 10 per cent of guaiaretic acid and 15 per cent of resin. Resin and the strained gum are sold for medicinal use, and some use in varnishes.

Gum mastic is a yellowish or greenish transparent resin obtained by incision of a type of balsam tree, *Pistacia lentiscus,* grown in the Mediterranean region. It is soluble in ether or acetone, almost entirely soluble in alcohol, and partly in oil of turpentine. About 2 per cent of volatile oil is present. It is used in medicine, dental cements, plasters, varnishes, lacquers, adhesives, chewing gum and incense.

Gum sandarac is a yellow, translucent, faintly aromatic resin obtained from a tree, *Callitris quadrivalvis*, growing in Morocco. It enters the market as brittle, elongated tears. Gum sandarac is soluble in alcohol, ether, amyl alcohol and hot aqueous alkalies. It is partially soluble in many solvents such as choloroform and turpentine. This gum contains about 1 per cent of volatile oil; the balance is largely complex acids. It is used in incense, varnish, lacquer and dental cement.

Gum scammony is a resin obtained by exudation or by alcohol extraction of the thick root of a twining species of *Convolvulus Scammonia* native to Asia Minor. It is an expensive material as compared with other resins, and is used in medicine as a purgative, hydragogue and cholagogue.

Benzoin, gum benzoin or **benzoin resin** is a mixed balsam and resin. **Siam benzoin** comes from Siam and nearby countries and is from the *Styrax benzoin* tree. It is of higher quality and usually lighter color than that from other sources. **Sumatra benzoin** is from Sumatra, Java and vicinity and is from other varieties of *Styrax*. It is definitely inferior and sells for 10-20 per cent of the price of the Siam grade. Benzoin enters the market as yellow to brown tears or compacted masses of tears, the centers usually being of lighter color than the surfaces. The U.S.P. grading requires that Siam Benzoin contain not less than 90 per cent of alcohol-soluble extractives, not over 0.5 per cent of acid-insoluble ash and not over 1 per cent of foreign organic matter. The Sumatra grade must have not less than 75 per cent of alcohol-soluble material and not over 1 per cent of acid-insoluble ash. Benzoin contains up to 40 per cent of free and combined benzoic and cinnamic acids, small amounts of vanillin and ethereal oils, and a resin esterified with benzoic acid. It is used medicinally and in cosmetics, perfumes, etc. Use may be as a preservative due to its benzoic acid content.

Tincture of benzoin is the solution obtained from 200 grams of benzoin in alcohol to make one liter. **Compound tincture of benzoin** correspondingly is made from 100 grams of benzoin, 20 grams of aloe, 80 grams of storax and 40 grams of Tolu balsam, made up to 1 liter with alcohol.

Podophyllin or **resin podophyllum** is an expensive resin extracted with alcohol from the root stock of the May apple or mandrake, *Podophyllum peltatum,* concentrated and precipitated with water and 0.1 per cent hydrochloric acid. The procedure for extraction is a U.S.P. standard. It occurs as a greenish yellow to brown powder or as small lumps, and darkens on exposure to light. The resin is very irritating to the eyes and to mucous membranes. It is soluble in alcohol with only a faint turbidity, and in aqueous alkalies. About 75 per cent dissolves in ether and 65 per cent in chloroform. The constitution is very complex. It is used in medicine as a cathartic and cholagogue.

Gum opium is a gum resin obtained as a milky liquid by incision of the unripe fruit of the opium poppy, *Papavar somniferum,* grown in various parts of eastern Europe, Asia and Asia Minor. The liquid dries to a brown mass. In the normal moist condition it contains around 10 per cent of anhydrous morphine, the U.S.P. standard requiring not less than 9.5 per cent. Codeine is also present with many nonnarcotic substances. The moist material is plastic but becomes hard and brittle or tough, on drying. It has a characteristic odor. The U.S.P. grade is sold in masses, which are generally flattened spheres with fragments of leaves adhering. It is used in medicine as a narcotic, sedative, anodyne, antispasmodic, hypnotic and diaphoretic, and for the preparation of alkaloids. **Granulated opium** is a U.S.P. product produced by drying gum opium below 70° C. and granulating, all passing a 16-mesh screen and not more than 10 per cent passing a 60-mesh screen. It is used medicinally. **Powdered opium** is a U.S.P. grade similarly prepared and reduced to a fine powder. It contains 10-10.5 per cent of anhydrous morphine. It is used medicinally. **Denarcotinized opium** or **deodorized opium** is powdered opium from which narcotine has been extracted with petroleum ether. It is used medicinally, avoiding some of the disagreeable effects of opium.

Camphor gum or **camphor** is a colorless or white crystalline solid with a characteristic pungent odor, slightly soluble in water but readily soluble in alcohol, ether or other organic solvents. Several products appear under the name of camphor, but it should be applied only to oxygenated derivatives of terpenes and sesquiterpenes. Structurally camphor is a ketone and differs from the usual gums in being crystalline. In use it is more closely related to other gums than to ketones. The most important is **Japan or laurel camphor** obtained by steam distillation of twigs of the camphor laurel, *Cinnamomum camphora,* which grows in several countries in the Far East. The distillate is separated into a liquid or camphor-oil fraction, and the solid camphor gum by fractional distillation, by freezing out the solid material or by chemical means. The crude camphor is purified by sublimation in the presence of quicklime and charcoal. **Borneo camphor, thymol camphor, mint camphor** and **Buchu camphor** are slightly different chemically from Japan camphor, and are obtained from other species of trees. **Synthetic camphor** has the same structure as Japan camphor and is prepared from the pinene of turpentine oil. **Artificial camphor** is pinene hydrochloride, an intermediate in the synthesis of camphor, having a camphor-like odor.

Natural camphor is sold in powder form, in slabs, and in tablets, the latter being the most expensive. Synthetic camphor is a little less expensive than the natural and is sold in powder form and in tablets. The U.S.P. grade includes natural and synthetic, and melts at 174-177°C. Camphor is used mostly as a plasticizer in making celluloid and other plastics. It is also used in making smokeless powder, and to some extent in medicine as a counterirritant and antiseptic.

Camphor monobromate is a colorless or white solid insoluble in water and slightly soluble in alcohol, ether or chloroform. It is prepared by the reaction of camphor with bromine. The U.S.P. IX product quoted is about three times as expensive as natural camphor. It is used in medicine as a sedative and antispasmodic.

Aloe or **aloes** is obtained as a dried juice from the leaves of various species of the *Aloe* plant, which belongs to the lily family. **Socotrine aloe** is from *Aloe perryi,* **Curacoa aloe** from *Aloe vera,* and **Cape aloe** from *Aloe ferox.* Aloe is sold in the form of orange to dark brown resin-like masses, according to its origin; Barbados, Cape, Curacao, Curacao-gourds and Socotrine. The grades differ widely in price. According to U.S.P. standards, aloe must not contain more than 4 per cent of ash nor 10 per cent of moisture, and must contain not less than 50 per cent of water-soluble material. Its uses are medicinal as a laxative, emmenagogue and bitter tonic.

Burgundy pitch is a yellow to brown brittle resin obtained as an exudation from Norway spruce, *Picea abies.* Synthetic mixtures having similar properties are also sold as **imitation Burgundy pitch,** because of the relatively high price of the natural product. A resin from silver pine is also sold as Burgundy pitch, but differs in that it is soluble in ether and chloroform, while true Burgundy pitch is only partially soluble in these solvents. Domestic and imported grades are quoted, the domestic being at approximately half the price of the imported. Burgundy pitch is soluble in alcohol, acetone or acetic acid. The aromatic material is used as an ingredient of medicinal plasters and has miscellaneous varied applications, including that of rubber compounding.

Natural musk is the dark brown to black dried secretion from the sac located under the skin of the abdomen of the male musk deer, *Moschus moschiferus.* The deer are native in Thibet and Northern Asia. The contents of musk are muskone, cholestrin, fats, waxes, etc. It is quoted as Tonquine in pods, the natural sacs, or at a higher price when removed and grained. Medically it is a nervine, anodyne, aphrodisiac, antispasmodic and stimulant. The major use is industrial as a fixative and odorant in perfumes. For industrial use synthetic musks are also quite generally used. The latter are classified with organic nitro compounds.

Castoreum or **castor** consists of the dried perineal glands with their secretions, obtained from the common beaver, *Castor fiber.* The follicles are in pairs of club-shaped wrinkled black sacs weighing 25-100 grams. The contents are brown, hard and friable. About half of the contents is soluble in alcohol. The odor is acrid and characteristic. The resin constitutes 40-70 per cent of the composition, with the balance consisting of organic acids, cholesterin, etc. A synthetic orange to brown creamy paste is sold at a price often higher than that of the natural product. Castoreum is used in medicine as an antispasmodic, emmenagogue, nervine and stimulant. A more important use is in perfumery as a fixative.

Civet is an unctuous yellow to brown solid with an unpleasant odor. It is secreted by glands at the posterior of the civet cat, *Viverra civetta,* native to Africa and the East Indies. The mixture is only partially soluble in organic solvents and is high in oils and resins. It is used as a perfume fixative.

Asafetida or **gum asafetida,** is a soft gum resin obtained from cuts in the living roots of various species of *Ferula* which grow in Persia, Turkestan and Afghanistan. The gum has an odor and taste similar to that of garlic. It gives a milky extract when triturated with water. The gum contains 6-17 per cent of ethereal oils, 40-60 per cent of resins, 25 per cent of water-soluble gums with some vanillin and ferulic acid. The U.S.P. standard requires not less than 50 per cent to be soluble in alcohol and not more than 15 per cent of acid-insoluble ash. Asafetida is sold in the form of tears or dark-colored masses, or in a more expensive powdered form. Uses are in medicine as an antispasmodic and nervine, and in the East as a condiment.

Gum ammoniac or **gum ammoniacum** is a gum resin exuded from the stems of the perennial ammoniac plant, *Dorema ammoniacum,* which grows in Persia, Northern India and Southern Siberia. The product appears in the form of opaque rounded tears. They are soft when warmed but brittle when cold. The outside is generally yellow to brown, the inside nearly white. The product also appears as irregular pieces which are usually darker in color. Gum ammoniac is partially soluble in water, alcohol or ether, and consists of a mixture of 65-70 per cent of resin, 1-2 per cent of volatile oil, and the balance, water-soluble gums, salicylic acid and resinotanol. It forms emulsions with water and is used medicinally as a diaphoretic, emmenagogue, diuretic, stimulant and expectorant, and in porcelain cements.

Gum olibanum or **frankincense** is a fragrant gum resin obtained from various Egyptian and East African *Boswellia* trees.

It contains 3-7 per cent of volatile oil, 60-70 per cent of resin, and 27-35 per cent of gum. Gum olibanum is sold in the form of siftings and tears. The term gum thus, is sometimes applied to this material but the present trade use applies that term to another product. The gum is used in making incense, fumigants, perfumery, and plasters.

Pine oleoresin, when separated from contaminants, is neutral as to reaction on metals, and noncrystallizing. It can be classified as a blend of rosin and turpentine, sometimes marketed as **gum thus.** That term is also applied to gum olibanum. The usual form is fused in barrels much the same as rosin.

Gum myrrh is a yellow to brown aromatic gum resin sold in the form of tears or irregular particles and obtained from the myrrh trees, *Commiphora abyssinica,* of East Africa and Arabia. It contains 2-8 per cent of volatile oil, 25-40 per cent of resin, myrrhin, and the balance largely gum. It has a characteristic odor and acrid taste. The U.S.P. grade is sold, a standard requiring 30 per cent solubility in alcohol and not more than 5 per cent of acid-insoluble ash. It is used in tonics, in dentrifices, perfumery, cosmetics, incense and for many miscellaneous purposes.

Gum kino is a red to black gum resin obtained from various trees growing in western Africa, East India, Ceylon and Bengal. Without purification, it is about 45 per cent alcohol-soluble and 80 per cent water-soluble. In 90 per cent alcohol it dissolves slowly and incompletely. Over 70 per cent is kinotannic acid, the balance largely gum. The U.S.P. grade contains not less than 60 per cent of alcohol-soluble extractives, and at least 75 per cent of water-soluble extractives. It has astringent properties, as would be expected from the tannin content, and is used in medicine, to a lesser extent in tanning and dyeing, and in textile treatments.

Gamboge or **gum gamboge** is a gum resin obtained from various related *Garcinia* trees grown in East India and China. The best grade is from Singapore and Canton. The gray to orange-brown gum becomes bright yellow when powdered, and is soluble in acetone, alcohols, benzene or ether. It contains 70-80 per cent of resin and 15-25 per cent of gum. Gamboge is sold in "pipe" and powdered form, for use in medicine, and as an artists' paint pigment.

Gum galbanum is a yellow to brown aromatic gum resin obtained from various species of *Ferula* growing in Persia. It contains 5-10 per cent of volatile oil, about 20 per cent of gum and about 60 per cent of resin. This gum resembles asafetida and is used in perfumery and in medicine.

Euphorbium or **gum euphorbium** is a yellow to brown, acrid gum resin obtained from *Euphorbia resinfera,* native to Morocco. The tears are soluble to about 60 per cent in alcohol, about 55 per cent in ether, about 32 per cent in water, and almost completely in glacial acetic acid. It contains about 25 per cent of calcium malate, the balance complex substances such as 40 per cent of euphorbone. Euphorbium is used externally as a vesicant, largely in veterinary medicine.

Gum elemi is an oleoresin obtained from *Canarium commune* and related trees of the Philippine Islands. It is soluble in hot alcohol, ether, turpentine or chloroform. Gum elemi enters the market as soft, yellowish, transparent, granular masses. When cold it is friable. It has a fragrant odor of a terpene nature and contains 20-30 per cent of volatile oil. The gum is used as a perfume fixative and in varnishes, lacquers, inks and related products. It is also used medicinally in plasters and ointments.

Oak-moss resin is light yellow in color and extracted from either of two varieties of lichens, *Evernia prumastri* or *Evernia furfuracca,* which grow on oak trees. It is obtained largely in France and Italy, and is used as a perfume fixative.

Rubber or **caoutchouc** is a polymeric hydrocarbon containing some resin, which enters the market as an elastic solid. It comes from various varieties of *Hevea* as **rubber latex,** a milky sap, and is closely related in use to the resins. While **latex** is a general term for the milky sap of a tree or shrub and nearly all types contain more or less rubber, the term by custom means that of the rubber tree. Rubber latex has many uses as an adhesive and impregnating agent as well as in the production of rubber articles by electrodeposition, dehydration on porous porcelain, etc. It enters the market as the natural latex containing 38-40 per cent of rubber, about 3 per cent of proteins, 4 per cent of resins and 0.5-1.0 per cent of ash. Ammonia has usually been added to prevent coagulation. Other prepared forms of latex have had the rubber prevulcanized, or have been concentrated to as much as 70 per cent rubber, usually with sodium soaps added to prevent coagulation.

Plantation rubber is from planted trees, the latex being usually coagulated with acetic acid, sulfuric acid or alum solution. It may also be smoked. Varieties reaching the market are smoked sheets, latex crepe, brown crepe, etc. **Wild rubber** is usually coagulated by heat, although crude chemical methods are sometimes used. Numerous varieties of Para, Caucho, African rubber, etc. enter the market. The wild may appear as balls or irregular pieces. The term of **hevea rubber** is often applied to the various forms of true rubber.

In general, plantation rubber is from the Malay States, Sumatra and Java, wild rubber from South America or Africa. Rubber is largely soluble in carbon bisulfide and swells in many organic solvents such as benzene. It is an important tonnage material for automobile tires, rubber mats, sanitary goods, etc. Such products are vulcanized with sulfur, relatively small amounts giving elastic and flexible products such as rubber bands or rubber gloves, large amounts of sulfur giving **hard rubber** or **ebonite** such as used in storage battery cases. All gradations are possible. In vulcanization, synthetic organic compounds, usually amine derivatives, are added as **vulcanization accelerators.** Other compounds added to prevent deterioration are known as **antioxidants.** The natural rubber contains proteins and resins which serve as natural antioxidants. In the coagulation of latex these are largely eliminated. They are still present in wild rubber obtained by the drying of rubber latex. Some rubber items such as bathing caps and aprons are of **acid-cured rubber** vulcanized by sulfur monochloride vapor.

Aside from sulfur, antioxidants and vulcanization-accelerators, commercial rubber articles usually contain pigments, often carbon black, and softeners such as stearic acid, pine oil, etc. Commercially **reclaimed rubber** is the residue when tire carcasses and other scrap rubbers are treated with sodium hydroxide solution under pressure to destroy cellulose fibers. This is worked on rolls with pine oil or other softeners to the consistency of natural rubber and used as an ingredient of rubber mixes. There are also other rubber reclaiming processes. A grade of reclaimed rubber containing cotton fibers is also an article of commerce.

Guayule rubber is not from latex but from a shrub growing in the desert regions of the southwestern United States, which yields the rubber as strands included within its stem. Guayule rubber is high in resin content as compared with hevea rubber and is used in compounding rubber mixes. From this, rubber shades off into a series of gums with high resin contents and usually some rubber hydrocarbons or related materials.

True synthetic rubber as such is not a commercial product, but varied related resinous materials are discussed as synthetic resins. Some materials imported in minor amounts are incorrectly called synthetic rubbers, incorrectly so because the composition is not identical with that of rubber. So-called rubber substitute or factice is discussed under fatty oils, from which it is derived.

Gutta percha is a term applied to a rubber-like substance produced by coagulation of the latex of *Palaquium gutta* which grows wild in Malaya, Sumatra and Borneo. It was formerly tapped from the tree but is now largely obtained by extraction from the leaves. The quantity of true gutta percha available is strictly limited and is classified as **red Macassar gutta percha.** Some comes from other varieties of the *Palaquium* family but often is from other species. Inferior varieties are **Gutta Siak** and **Gutta Soh.** Their inferior quality causes them to sell at less than one-quarter the price of red Macassar in normal times. Some has been collected by natives and reconditioned. The term **inferior gutta** is sometimes used to designate these types. True gutta percha is used largely for cable insulation. Either the true or inferior gutta is used in golf balls, as tissue for tailoring, and in other ways as a thermoplastic adhesive, in cements and sealing compounds and for compounding with rubber.

Balata is a rubber-like gum distinct from gutta percha but often confused with it. It comes from northern South America from the latex of *Mimusops globosa.* Some from Panama is from the *Mimusops darienensis.* Grades are Cindad Bolivar block, Manaos block, Surinam sheets and amber sheets. Prices are higher than for inferior gutta percha but much lower than for true gutta percha. It is all from wild trees and is used in waterproof belting where the temperature is not high. Balata is more of European than American interest, rubber having largely replaced it here. Other uses are for packing, gaskets, etc.

Chicle is another rubber-like gum from the latex of *Achras zapota* or *Achras chicle,* a wild tree of Central America. Inferior grades of chicle from other areas are probably from other types of trees. The use is largely in chewing gum, where so far as possible, substitutes replace the true chicle because of price.

Gum Pontianak or **jelutong** is a rubber-like gum from the latex of various trees. It has an actual rubber content of about 20 per cent. This gum comes from the Pacific area and has at times been worked to remove resins and yield rubber. Commercially it is sold as pressed blocks. The gum is also mixed with inferior gutta perchas. Use is largely in chewing gum to replace part of the chicle.

Canada balsam, fir balsam or **Canada turpentine,** an oleoresin, is obtained from the balsam fir tree, *Abies balsamae.* The yellow to greenish liquid has a pine-like odor, and solidifies to a transparent semisolid mass. It gradually solidifies on exposure to the air but remains transparent. It is soluble in ether, chloroform, benzene, ethyl acetate, and some oils. Grades sold are Canada and Oregon. The latter is sometimes called **Oregon balsam.** The former is expensive, the latter relatively inexpensive. Canada and Oregon balsams are used in medicine and as a transparent cement, particularly in the preparation of optical goods such as the mounting of lenses and instrument parts, and in preparation of microscope slides. Some is used in lacquers. The product is sometimes incorrectly confused with balm of Gilead, a distinctly different balsam.

Mecca balsam or **balm of Gilead** is a balsam obtained from the twigs of a small evergreen, *Balsamodendron gileadense*, which grows on the shores of the Red Sea. The yellow to green product has a fragrant odor and is soluble in alcohol, benzol, acetone or chloroform. It is sold as buds for use in perfumes.

Copaiba balsam is an oleoresin obtained from several South American trees of the *Copaifera* family. The viscous yellow to brown liquid is transparent and has an aromatic odor. It may have a slight greenish fluorescence. This balsam is soluble in benzol, ether, chloroform, carbon bisulfide and oils. It dissolves in absolute alcohol but only partially in 95 per cent alcohol, and in an equal volume of petroleum ether, but is partially precipitated by more petroleum ether. The ingredients are of complex structure. Usual grades are Para, and South American U.S.P., mainly imported from Brazil. The U.S.P. grade has a specific gravity of 0.930-0.995 at 25°C. Aside from medicinal uses it appears in special varnishes and in the manufacture of photographic and tracing papers. **Balsam Gurjun** or **East Indian Copaiba** is an oleoresin of related composition from eastern India and Burma, used for similar purposes. It differs in being incompletely soluble in ether and carbon bisulfide.

Storax or **styrax** is a balsam obtained from the bark of trees grown in Asia Minor and imported from Turkey or Italy. That from *Liquidamber orientalis* is known in commerce as **Levant storax**; that from *Liquidamber styraciflua* is known as **American storax.** A purified grade sometimes sold, is prepared by dissolving one of the grades of storax in alcohol, filtering to remove insoluble debris and evaporating the alcohol from the filtrate. The grayish brown liquid has a fragrant odor, and contains resin, styrene or styrol, cinnamic acid, ethyl cinnamate, ethyl vanillin and related compounds. The Levant storax deposits a heavy brown layer on standing, American storax a semisolid mass which softens on gentle warming. Storax is heavier than water and is usually incompletely soluble in warm alcohol, acetone, carbon bisulfide or ether. There are U.S.P. grades of both types meeting specified tests for purity. Storax is used in medicine, in fumigants, and in perfumery as a fixative and odorant. Storax is also a source of some fine organic chemicals such as a special grade of cinnamic acid.

Tolu balsam is a balsam obtained from a South American tree, *Toluifera balsamum*, as a brown or yellowish brown plastic solid which is transparent in thin layers. Imports are largely from Colombia. It becomes brittle when old, when dried, or at low temperatures. The odor is aromatic, resembling that of vanillin. It is nearly insoluble in water or petroleum ether but soluble in alcohol, chloroform or ether. Tolu balsam is largely soluble in aqueous alkalies. It contains about 8 per cent of benzoic acid, 12-15 per cent of cinnamic acid, vanillin, resins and complex benzoates and cinnamates. This balsam is used in medicine, perfumery, chewing gum, confectionery and fumigants. There is a U.S.P. specification. **Tincture of tolu balsam** is a U.S.P. preparation containing 200 grams of balsam per liter in alcohol. **Syrup of tolu balsam** is also a U.S.P. preparation, containing 50 cc. of tincture and 820 grams of sugar per liter. It is made with 10 grams of magnesium carbonate, which is filtered off, to clarify it.

Peru balsam or **Peruvian balsam** is a balsam obtained from the *Toluifera-pereirae* of Central America. It is imported mainly from Salvador and Nicaragua. The dark-colored liquid resembles molasses in appearance. In thin layers it is reddish brown and transparent. The odor resembles that of vanilla. It does not harden in the air and is soluble in alcohol, chloroform and glacial acetic acid with only slight opalescence, and incompletely soluble in ether and petroleum ether. Peru balsam contains 50 to 60 per cent of cinnamein, about 28 per cent of resin, together with benzyl esters of benzoic and cinnamic acids, styracene, vanillin, etc. It is used medicinally according to U.S.P. grading of specific gravity 1.15-1.17 at 25°C. Other uses are in perfumery and confectionery manufacture.

Venice turpentime or **larch turpentine** is a yellow to green viscous oleoresin with a pleasant aromatic odor, obtained by distillation from varieties of the European larch. It becomes hard and brittle on prolonged exposure to the air. **Artificial Venice turpentine,** sometimes offered, consists of a mixture of rosin and oil of turpentine and is similar to pine oleoresin. It is readily soluble in ether, acetone, acetic acid or aqueous alkalies, slowly in alcohol. True Venice turpentine consists chiefly of volatile oil and resin. Both are used in making varnishes, sealing wax and plasters, and for lithographic work.

CHAPTER XXXV

SYNTHETIC RESINS

As indicated by the name, **synthetic resins** are purely synthetic products having the general properties of natural resins. Since their production is under scientific control, they are more uniform in composition and usually superior to the natural resins in solubility, hardness, gloss, color and stability in solution. Various modifications of composition and of methods of production are possible, so that desirable properties can be enhanced and improvements made to meet particular needs in industry. Hundreds of these resins are on the market, with continual progress, development and change still going on. All fall into a limited number of classes.

Synthetic varnish resins are a class of synthetic resins which can be kettled with oils, usually linseed oil or Chinawood oil to produce materials which, cut in suitable solvents, serve as varnishes. There has been a marked trend for the past decade to replace natural resins with synthetics for this purpose.

Synthetic molding resins are synthetic resins in a form which can be molded and insolubilized by heat and pressure, reaching the public in the form of commercial parts, and as decorative articles. These normally contain a large amount of inert filler such as wood flour. This application of synthetic resins is to only a small extent parallel to uses of natural resins, competing rather with hard rubber, pottery, metals, etc.

The field of synthetic resins is complicated by the use of resin-impregnated materials. **Resin-impregnated paper** serves as an adhesive, particularly in laminating wood under heat and pressure. A compacted mass of several sheets of resin-impregnated paper or cloth may replace a sheet of synthetic resin alone.

While synthetic resins are often described as insoluble in water, acids, alkalies and solvents, this is purely a relative description. Many are attacked by alkali and possess some solubility in organic solvents.

Chemical classification of synthetic resins is difficult, since they are all sold under trade names. In some cases the nature of the composition is not disclosed and in few cases is it given in quantitative terms. Some companies sell several resins which may be entirely different in type, under the same trade name. Such products are designated by letters or numbers or a combination of the two. Necessarily products are referred to by current trade names.

Resins of the **phenol-formaldehyde** type represent the first synthetic resins that were commercially successful, sold under the name of Bakelite. The basic patents have now expired and these resins are also made by other manufacturers. They are produced by condensing phenolic substances such as phenols and cresols with formaldehyde or other suitable aldehyde. Phenolic resins may be modified by dispersing them at the time of manufacture in natural or esterified resins. This makes them oil-soluble so that they can be used in producing varnishes and gloss printing inks. Phenolic resins modified with drying oils become insoluble and infusible on heating, and are applied as varnishes. Straight phenolic resins, similarly heat-reactive, are cast, by pouring the liquid resin into molds and allowing it to harden under heat. Properly modified, the resins forming the cast block or rod can be worked into finished articles of any shape by the ordinary tooling operations. These compete with molded resins containing filler. Large acid-proof industrial equipment is made by filling or extending the resin with asbestos flock or other inert material. The phenolic resins still represent the largest class of synthetic resins and find many varied uses. In general, except in varnishes, they are originally dark or darken in the light.

Bakelite resins are usually phenol-formaldehyde in type, offered in various forms and with various properties. They are used in paints, varnishes, enamels, laminated products, molded, cast and machined articles. Some of the **Beckacite** resins belong to the modified phenol-aldehyde type and are used in oil varnishes. **Durez** resins are 100 per cent phenolic resins used in varnishes, enamels and molded products. **Para-dura** is a similar type of resin used in varnish and lacquer. **Durite** is a general varnish resin. **Locto** is also a phenol-formaldehyde resin. **Paranol** resins are modified phenolic products used in varnishes. **Varcum** resins are phenol-aldehydes used in varnishes and other coatings and as impregnating materials. **Catalin** is a molded phenolic resin, as are also **Marblette** and **Haveg.** **Revolite** is a cloth, coated with modified phenolic resin.

Alkyd resins, glyptal resins or **phthalic-glyceride** resins are terms which cover condensation products made by the reaction of polybasic acids or anhydrides such as phthalic, succinic or maleic acids, with polyhydric alcohols such as glycerine, sorbitol, mannitol, etc. These are combined under different conditions and usually modified in various proportions with fatty or natural resin acids. Their major field is for baking enamels. When monobasic acids are used to change the character of phthalic glycerides, the products are known as **Rezyls.**

A modification of alkyd resins other than with resin acids and fatty acids, is with drying oils. The presence of natural resin acids tends to make the product hard and brittle. Fatty acids make it softer and more gummy, yielding a product suitable for use with nitrocellulose in lacquers. Drying oils give an oxidizing type of resin which produces hard solid films, a property of value in printing inks and varnish bases. When modified alkyd resins are combined with phenols, many variations are possible, covering a wide field of usefulness. Some of the **Beckacite** resins are of the alkyd type and are used in varnishes and lacquers. **Beckosol** is sold in several types, such as air-drying finishes, paints and enamels, low-bake and high-bake finishes, plasticizers, etc. **Esterol** is the name of a group of alkyd resins used in varnishes, lacquers, paints and enamels. **Lewisol** resins are used with nitrocellulose in lacquers, in oil varnishes, and with nitrocellulose alone as in making sealers. **Duraplex** is used in coating materials.

Urea-formaldehyde resins are made by the condensation of these compounds. They are used in molding compositions and appear in a wide variety of colors of good stability and shade.

Examples are **Unyte, Plaskon** and **Beetle.** This type of resin is also applied to cloth to make it crease-proof, and is added to nitrocellulose lacquers. Other uses are as closures, buttons, etc., because of greater mechanical strength than that possessed by phenolic resins.

Vinyl resins are made by the co-polymerization of vinyl chloride and vinyl acetate, the proportions of which vary in different resins. The usual products are available as molding powders. A high vinyl-acetate resin is tough and flexible and is used in coating materials. When treated with aldehydes these resins become harder. Examples of the latter are the **Alvars,** used in spirit varnishes, enamels, lacquers, cements, adhesives and plastics. **Vinylite** is a vinyl chloride-vinyl acetate resin used for making flexible sound records, artificial dentures, coatings, and in spirit varnish. **Mowolith** and **Gelva** are vinyl acetate polymers without appreciable amounts of vinyl chloride.

Coumarone-indene resins or *para*-**cumarone resins** are produced by the polymerization of these chemical compounds, obtained from coal-tar light-oil distillates. The polymerizing agent is heat or acid. They are lemon-yellow to reddish brown amorphous mixtures from which volatile oils have been removed by distillation. *Para*-indene, *meta*-styrene and similar substances may be present in the mixture. They decompose on heating to 250° C. Some are soluble in ether, coal-tar and petroleum solvents, turpentine, acetone, ether or carbon tetrachloride. These resins are neutral, resistant to alkalies and dilute acids, brine, etc. They are frequently used to modify the properties of other synthetic resins. **Cumar resins, Neville resins** and **Nevillac resins** are of this type. They are sold in varied grades by letter which indicate hardness or melting point, and degree of polymerization. The melting points vary from 10° to 160° C. Some grades are subdivided by numbers ½, 1, 1½, etc., indicating color. A lighter color, or a harder resin, in general commands a higher price. These resins are used in varnishes, enamels, plastics, printing inks, insulating compounds, as softeners in compounding rubber, in adhesives and in chewing gum. Some is used as cold-cut varnish, comparable in some ways to spirit varnish.

Polystyrene is made by polymerization of the hydrocarbon, styrene. It is water-white in color, is very tough, and has the highest insulating power of any available synthetic resin. Its use is limited by high price. Examples of this type of resin are **Resoglaz, Trolitul, Victron** and **Tepperite,** used in spirit varnish, and the latter product in dentures.

Petroleum resins are neutral hydrocarbon resins made by treating unsaturated petroleum fractions with aluminum chloride. These resins accelerate the drying of tung oil. **Dayton synthetic resins** are used in varnishes, paints and enamels. They increase resistance to water, acid and alkali.

Modified natural resins consist of natural resins or resin acids, usually modified with glycerine. The resin acid reacts with glycerine to form esters. Manufacture can be controlled to vary the product with respect to color, hardness, acidity and solubility. These modified resins give greater durability and general resistance to a varnish film than does the ordinary gum. A disadvantage for some purposes is a tendency toward softness and tackiness. **Ester gum** is produced by esterifying the abietic acid of rosin with glycerine. Methyl and ethyl esters can also be produced. It is soluble in oils or turpentine, and is used in varnishes and lacquers.

Amberol resins are phenol-formaldehyde resins in type, but are modified with natural resins. They are used in oil varnishes and in nitrocellulose sealers. **Abalyn,** an abietic acid ester, is used as a plasticizer for nitrocellulose lacquers. **Hercolyn** is used as a plasticizer for nitrocellulose. **Paramet ester** is used in varnish and lacquer. **Flat gum** belongs in this class but contains a flatting agent. **Imperial gum** is used in nitrocellulose and oil coatings. **Kopols** are fused or esterified copal, used in floor varnish and as an enamel vehicle. **Beckopol** is a phenolic copal combination used in extremely hard varnishes of the rubbing and polishing type. **Paraplex** is glycol-sebacate, and represents a group of plasticizing resins for nitrocellulose lacquers.

Rubber resin made by the chemical treatment of rubber is acid- and alkali-resistant. The milled and unmilled product is sold under the name of **Pliolite.** It is used in coatings and for the impregnation of materials. In sheet form it is **Pliofilm.**

Rubber replacents, if neither synthetic rubber nor synthetic resins, are closely related. They are not termed rubber substitutes because that name is applied in the trade to sulfurized oil, factice. Polymerization of monovinylacetylene with hydrochloric acid gives **chloroprene,** which can be polymerized to a rubber replacent which is very resistant to oils. This was first known as **Duprene,** later as **Neoprene.** It is more expensive than rubber but has the merit of greater solvent resistance. Polymerization of ethylene dichloride with an alkaline polysulfide produces a polyethylene sulfide. While structurally unlike rubber, the product is an elastic, rubber-like material, resistant to solvents and oils but of unpleasant odor. It is sold as **Thiokol.**

Chlorinated rubber may be considered a closely related product. It has unusually good adhesive properties, is noninflammable, is resistant to water, acids and alkalies and is a nonconductor of electricity. One name used for a time was **Tornesite** but that name has been abandoned.

Chlorinated diphenyl is of variable nature from a clear colorless liquid to a yellow brittle resin. It is used as a fireproof coating and as a dielectric under the name of **Arochlor,** of which there are numerous varieties.

CHAPTER XXXVI

CARBOHYDRATES

There is a large group of commercial products which are compounds of carbon, hydrogen and oxygen combined in very nearly the same proportions, but varying in internal structure, and differing widely in properties. They are characterized by the presence of a number of hydroxyl groups. Generically, the group is known as **carbohydrates** and includes cellulose, starch, dextrins and all of the sugars. Naturally, with such diverse properties, compounds of this class have many different uses.

Cellulose is a major ingredient of the fibrous structure of plants and trees, accompanied by a number of other substances. It reaches industry not only in the massive form of lumber, but also in chip form, ground as wood flour, and in the form of plant fibers. The purest form of cellulose found in nature is in cotton. For this reason **cotton** was formerly used as a source of pure cellulose in many industries, where improvements in the processing of wood pulp now permit the use of cellulose from wood. An example is in the rayon industry.

Chemically, cellulose is a carbohydrate having the formula $(C_6H_{10}O_5)_n$. This is substantiated by the fact that cellulose hydrolyzes to give glucose, $C_6H_{12}O_6$, as a final product. The structural formula is still open to question, there being a possibility that no one formula will suffice. X-ray studies show that cellulose aggregates consist of crystallites, which are not perfect crystals but which might be said to exist as the first step in a crystallization process. The arrangement in crystallite form is the same for cotton, ramie and wood. However, cellulose from these sources differs in properties, and it may be that these differences relate to differences of crystallite arrangement, more particularly with respect to fiber axis.

Cellulose is insoluble in the usual solvents but dissolves readily in an ammoniacal solution of copper hydroxide, called Schweitzer's reagent, and in concentrated solutions of salts such as zinc chloride and calcium thiocyanate. It is unaffected by moist chlorine, and as this converts nearly all of the materials which accompany cellulose into soluble substances, that property provides a convenient method for its purification.

Wood pulp is prepared mechanically or chemically from pulp wood. By the mechanical process the wood is ground wet against a grindstone, without removal of the natural incrustants or lignins which always accompany cellulose in wood. This **mechanical pulp** is of an inferior grade, suitable only for the manufacture of newsprint and other low-grade products.

There are three chemical processes for the removal of incrustants from wood—the soda, sulfate, and the bisulfite processes. The wood is cut up into logs, de-barked, and converted into chips by revolving cutters, and the chips passed between rollers. For **soda pulp** the chips are boiled with caustic soda solution under pressure. **Sulfate pulp** or **kraft pulp** is similarly made, using sodium sulfate solution instead of caustic soda. The yield is greater and the fiber stronger, but the pulp is normally a dark brown. For **sulfite pulp** a solution of sulfur dioxide is used, to which lime or magnesia is added in a quantity insufficient for complete neutralization. The sulfite process gives pulp of the lighest color and highest price. This special grade of pulp is characterized by a high content of alkali-resistant cellulose or *alpha*-cellulose, and a very low ash content. A bleached grade is often sold.

Mechanical and chemical wood pulps are produced in mills adjoining the forests of the wood-growing countries, and either converted into products there, or sent to all parts of the world for use in paper making and in other industries. Wood pulp is cut into sheets and baled for shipping, and can best be visualized as a thick, soft cardboard. This is readily broken down with water and by beating to give a pulp for incorporation into various products. **Pulp wood** is also an article of commerce in the form of sections of trees about 2-5 feet in length.

Wood flour is finely pulverized wood, as commercially available. It is obtained by grinding wood in various types of mills. The flour is then drawn or blown off and screened. It is used as a filler or absorbent in the production of a variety of products, such as linoleum, dynamite, phenol-formaldehyde resinoids, composition flooring, drying and polishing agents, hand soaps, in fur cleaning, etc. Many grades from hard and soft woods are available, of which domestic fine, domestic standard, imported 40-60 mesh, 70-80 mesh, 100 mesh and 200 mesh are representative. The price goes up rapidly as finer grades are required.

Wood waste in the form of shavings, splinters, trimmings and edgings from saw mills, constitute the bulk of the raw material used in making a **processed wood.** The wood chips are subjected to a steam pressure of 1,000 pounds per square inch and then discharged from the retort. They expand or explode immediately, owing to the high internal pressure. This completely ruptures the chip and produces a mass of long fiber bundles. These fibers are then felted together in the form of a mat which is cut into standard length and pressed into boards.

Products produced in this way from wood chips serve various constructional purposes. **Insulation board** is used for insulation against heat or cold and for its sound-deadening properties. **Insulating lath** has essentially the same characteristics and serves as a plaster base. **Quarterboard** is stronger and more rigid than the insulation material. **Pressed wood,** another of these commercial products, is an extremely hard, dense board with a very high tensile strength. It is used to replace ordinary wood as a building material. The light weight, smooth surface and large area make it particularly valuable for use in concrete forms. Bathroom and flooring tiles, blackboards and many other items are produced by application of special surface finishes to forms of processed wood.

Bagasse is the fiber remaining after the sugar has been extracted from sugar cane. This type of fiber is very tough. It contains multitudes of tiny air cells, which makes it excellent insulating material. Bagasse is used in the manufacture of various types of building materials, such as building board, lath, sheathing, tile board, panel board, roof-insulation board, etc., much as described for processed wood. The fibers are freed of residual sugar, felted together in huge machines, pressed into sheet form, and sawed into boards of stock sizes. During the manufacturing process, the material is waterproofed and treated to resist damage by fungus growth, dry rot and the attack of termites, a type of white ant known for their destructive attack on wood.

Rag paper is high in cellulose content. **Washed linen** is largely cellulose. Numerous grades of rags are sold for use as **paper stock.** Ground and floated, these rags become **cotton flock,** used as a finish on rubberized fabrics. **Jute** and **hemp** are lower in cellulose content. The usual grades of **paper** contain much clay and alumina as filling agents and glue or casein as binders for the finishes, in additon to cellulose fiber.

Low-grade cellulose is produced by reworking old paper, de-inked newspapers, etc. It is used for boxwood, wrapping paper and the molding of papier items. **Papier-maché** is a composition of cellulose, glue, rosin, fillers, etc., used for the manufacture of moulded items. The various commercial forms of cellulose as paper range from tissue, paper towels and newsprint to kraft paper and paper board on the one hand, and fine writing and ledger papers on the other. Much of the raw material of paper is old paper, such as newspapers used in making boxboard. Old rope and bagging forms stock which is used for heavy fiber board.

Hydrated cellulose or **hydrocellulose** is cellulose associated with more or less water to form a swollen or gelatinous mass. It is produced in a number of ways: By mechanical pulverization and agitation with water, which is the method used industrially in the papermaker's "beater"; by the action of strong solutions of salts such as zinc chloride, or by cuprammonium solution, which are the methods used for making vulcanized fiber and cuprammonium silk; by the action of strong solutions of alkalies, which is the mercerizing process used in the cotton textile industries, and is also the first step in the making of viscose; by the action of strong solutions of acids, which is the process of parchmentizing paper; by regenerating cellulose from its esters, which is the process of making rayon. Apparently water taken up by cellulose is held physically by a process of imbibition. However, the terms hydrated cellulose and hydrocellulose are often used inexactly to refer to any material composed of cellulose combined physically or chemically with more than the original proportion of water, or more than 8-12 per cent.

Although cotton cellulose is remarkably resistant to dilute alkalies, the fiber swells in contact with 15 to 20 per cent caustic-soda solution, and when stretched simultaneously, becomes lustrous or mercerized. Acids act on cellulose at first, to hydrate it, and in stronger solutions, to hydrolyze it into dextrins and finally glucose. Oxidizing agents such as chromic acid, permanganates, hypochlorites, hydrogen peroxide and even air act on cellulose in the presence of moisture and certain salts, or under the influence of strong sunlight, to form **oxycellulose.** The latter contains free aldehydic groups and disintegrates fairly readily, with the formation of carbonic and oxalic acids.

Under controlled conditions cellulose reacts with acids to form **cellulose esters,** when it behaves like a tri-hydric alcohol. Examples are the formation of nitrocellulose of various degrees of nitration, and of cellulose acetate. Both are true organic esters described as such in another chapter.

Another industrially important cellulose compound is formed by reaction with caustic soda solution and carbon disulfide, called **cellulose xanthate.** Its solution is **viscose.** This is used in the process of making rayon, in which it is converted to cellulose again. Other products similarly made from viscose are **cellophane** and similar transparent wrapping tissues. Cellophane is a generic term for such wrapping materials made from viscose, rather than a trade name. Viscose is used as a sizing for fabrics such as artist's canvas.

Cellulose ethers as well as esters, can be prepared from cellulose. The cost of producing ethers has been relatively great, which has prevented their utilization by industry in competition with the cheaper esters. **Methyl cellulose** and **ethyl cellulose** have however become important in recent years. These ethers can be produced with varying solubilities, such as ethers soluble in cold water, soluble in hot water but not in cold, etc.

Pure cellulose is easily prepared from cotton by the prolonged boiling of the raw material with a 1 per cent solution of caustic soda, subsequent treatment with dilute acetic acid, and repeated washing with distilled water. Its analysis will then be about 99.8 per cent of cellulose and 0.05 per cent of ash. The material obtained in this way is regarded as standard cellulose. Chemical **filter paper** is practically pure cellulose, especially if it has been further treated to reduce ash. Cellulose of a high degree of purity is an article of commerce in the form of sheets of wood pulp. Cellulose exists in three forms, classed arbitrarily as *alpha*-**cellulose,** *beta*-**cellulose** and *gamma*-**cellulose.** Of these, *alpha*-cellulose is insoluble in 17.5 per cent caustic soda solution. *Beta*-cellulose is soluble in 17.5 per cent caustic soda but insoluble in dilute acetic acid. *Gamma*-cellulose is soluble both in 17.5 per cent caustic soda solution and in dilute acetic acid. These are merely general classifications of types of cellulose, not of definitely different chemical individuals.

Starch occurs very abundantly in the vegetable kingdom, as it is found stored in practically all plants. It may be in the root or tuber as in the potato, or in a head of grain, as in cereals like wheat, oats and corn, or in the stalk as in sago. Starch has a very complex structure, its formula usually being written $(C_6H_{10}O_5)_y$, where y is a number of the order of 50. Such a formula ignores the presence of some phosphorus in starch as a minor ingredient. Although the proportions of carbon, hydrogen and oxygen in cellulose and in starch are similar, the starch molecule is much smaller and much more reactive than the cellulose molecule. This is shown by the much greater ease of acid-hydrolysis of starch, as contrasted with cellulose.

With the aid of chlorophyll and under the influence of sunlight, the plant builds up this complex substance from two simple compounds, water and the carbon dioxide in the air. Pure starch is made up of minute granules, the shape, size, and appearance of which differ according to the plant in which the starch had its origin. When starch is mixed with cold water, in which it is insoluble, it forms a paste which sets to a solid mass on standing. When heated with water or when treated with dilute acid, the granules burst and the starch molecule hydrolyzes to a greater or lesser degree, giving soluble starch. Other forms of soluble starch are produced by heating with dilute alkali or by treating with chlorine. Starch is identified by a very sensitive reaction in which, when heated with water, it forms a blue color with an aqueous potassium iodide solution of iodine.

When starch is hydrolyzed, the large molecule breaks down into somewhat simpler ones. First dextrins are formed, their composition and properties depending on the stage of hydrolysis. Dextrins in turn break down to maltose, a disaccharide. Maltose reacts with one molecule of water to form two molecules of glucose. This progressive hydrolysis or reaction with water is brought about slowly by boiling, and more rapidly by treatment with dilute acid or by enzyme action. Plants themselves contain enzymes or natural catalysts for converting starch to sugar. Thus starch is manufactured in the leaves, where the chlorophyll is found, converted by enzyme action into sugars which are soluble in the cell sap, and carried off to the roots or seeds, where the sugars are changed back to starch for storage.

Starch is isolated from corn, barley, oats, rye, potatoes, rice, millet, peas, lentils, arrowroot, tapioca, yam, sago and wheat. We are accustomed to thinking of starches and sugars as forming an important part of our diet, but they have many other uses besides that of food. The commercial grades are selected largely according to availability, **potato starch** being most important in continental Europe, **corn starch** in the United States.

Roots and tubers are cleaned and then cut up and grated to a fine pulp by machine. Vegetable fiber is separated by washing the pulp on sieves. The starch liquor is allowed to stand in vats to settle out sand and sediment. It is then filtered through silk and allowed to pass slowly over shallow wooden troughs, where the starch settles out and impurities pass off with the water. The white starch is washed from the troughs by a jet of water and passed through filter presses or extractors to remove all but 40-45 per cent of water.

Cereals may contain other compounds besides starch, which have to be removed. Protein in rice is made soluble by treatment with dilute caustic soda solution. Corn contains protein and an oil-containing germ. The corn is steeped for a few days in warm water containing 1 per cent of sulfur dioxide, ground up, diluted with water and passed through a V-shaped tank where the germs float to the surface and are skimmed off. The protein or gluten is dissolved in dilute caustic soda solution and thus separated from the insoluble starch. After further treatment, starch from this or from other sources is dried at a low temperature to prevent gelatination, sometimes *in vacuo* and sometimes by a continuous current of warm air.

Raw starch is sold according to the raw material from which it is made. Corn starch is sold as both **pearl starch,** a granular form, and as powdered. The latter is slightly more expensive. Potato starch is sold as domestic and imported. **Rice starch** is produced domestically. Wheat starch is offered as **thick-boiling starch,** which gives a heavier paste for a given starch content. **Laundry starch** is usually raw corn starch, often sold in lump form. It is first shaped into blocks by letting the starch liquor drain in boxes having perforated bottoms covered with filter cloths. The blocks are cut into sections and partly dried in a warm chamber. The brown crust which forms is scraped off, the blocks wrapped in paper and allowed to dry very slowly. The blocks break up of themselves into irregularly shaped forms termed "crystals" by the trade. Starches are also used for the manufacture of glucose, in paper sizings, in adhesives, in cosmetics, and as fillers in varied food products.

Sago is a granulated or ground starch prepared from the crushed and washed pith of the sago palm, *Metroxylon laeve* or *Metroxylon rumphii*, and from the trunks of several other palms and cycads which grow in the East Indies and the Philippines. When finely powdered it is **sago flour.** The uses parallel those of other starches, as a textile sizing and in the manufacture or preparation of food products. A form of pudding from it is particularly well known.

Tapioca starch is the starch from the **Brazilian arrowroot,** usually *Manihot utilissima.* It is also called **cassava starch,** and the roots from which it is produced, cassava roots. In finely ground form it is known as **tapioca flour,** in larger granules, usually of uniform size, it is **tapioca.** The uses are similar to those of other starches, and include in the tropics, manufacture of cassava bread from the flour.

Iodized starch or **starch iodide** is a dark-colored starch powder containing 2 per cent of iodine. It is used in medicine as a disinfectant and internal and external antiseptic. The British pharmacopoeia increases the iodine content to 5 per cent.

Inulin is a tasteless, white semicrystalline polysaccharide closely resembling starch. Its formula is written $(C_6H_{10}O_5)_{6n}$. Inulin occurs in the tuber of the Jerusalem artichoke, as well as in other plants of the *Compositae* family. It is sparingly soluble in cold water and very soluble in hot water. It differs from starch in giving a yellow instead of a blue color with iodine. When heated with water or with dilute acid, it is hydrolyzed to levulose. Inulin is used as a carbohydrate for diabetics, as levulose appears to be assimilable by the digestive system when dextrose is not.

Thin-boiling starch or **soluble starch** is a name for products obtained by a controlled hydrolysis of starch. They are produced by acid treatment at a definite pH with temperature control. Since the procedure represents a mild degree of hydrolysis the products may contain some dextrins.

Chlorinated starch or **oxidized starch** represents a further degree of hydrolysis and is usually obtained by treatment with sodium hypochlorite.

Dextrins or **British gums** give a red-brown instead of a blue color with iodine and therefore represent a complete breaking up of the starch molecule into somewhat smaller aggregates. Dextrins are sometimes called **vegetable glues.** They are mixtures of compounds produced by heating dry starch with catalysts, usually a small amount of acid. Dextrins dissolve in water to give sticky solutions, used as adhesives of various kinds, and as sizing for inexpensive grades of the type of cotton material known as organdy. Dextrins are sold according to the starch from which they are prepared, as potato, tapioca, etc. **Corn dextrin** and **potato dextrin** are sold in both canary and white grades.

There are probably thousands of commercial products which come under the heading of starches and dextrins, obtained from corn, tapioca, potatoes, etc. They vary in their properties according to the method of preparation. Frequently the method is adjusted to meet the specific requirements of an individual textile manufacture who uses these products very extensively as sizing, filling and finishing agents. Similarly, those using adhesives may specify certain qualifications to meet their own particular needs. Bookbinders, manufacturers of boxes, of dolls, labels, linoleum, luggage, paste, toys, and various food products, are among the many who use this type of product.

Sugar usually is a term used to mean **sucrose,** $C_{12}H_{22}O_{11}$, although the name covers many individual compounds having distinct properties, such as dextrose or grape sugar, fructose or levulose, lactose or milk sugar, maltose or malt sugar, etc. Sucrose occurs abundantly in plants and is extracted commercially from sugar cane, sugar beet, sorghum grass and other sources.

Sugar cane is a form of grass which grows to a height of 10-20 feet. It requires a moist and warm climate. The canes are grown from cuttings from a stalk of mature cane and harvested by cutting the cane at the ground level. Several crops grow from each planting. The green tops are removed and the stalks cut to lengths of 3-4 feet and sent to the factory for prompt crushing. The stalks average a content of 13 per cent of sugar. A record crop in Java gave 42 tons of canes per acre.

The **sugar beet** belongs to the same family as the red garden beet but the modern sugar beet was evolved from a white variety. By gradual selection the sucrose content was increased from about 5 per cent to a possible 20 per cent, with an average of 16 per cent. A record corp produced in Germany gave 12 tons of washed beets per acre. The refined product from either cane or beet has equal sweetening power, contains over 99.8 per cent of sucrose, and cannot be distinguished by chemical analysis.

Raw sugar or **centrifugal sugar** is the first solid or crude product. Cane sugar is manufactured by passing the canes through a crusher and then between successive sets of rollers which squeeze out the juice. Pressures of 250 to 500 tons are used and less than 2 per cent of juice remains in the exhausted cane. The extracted juice is a dark, opaque liquid having an acid reaction. As it was diluted with water during the extraction process, it contains from 12 to 16 per cent of dissolved sucrose, as well as various kinds of impurities.

Chemical treatment is necessary to neutralize the acidity, to remove suspended and dissolved impurities, and to remove coloring matter. Such purification must be carried out in a manner to avoid the hydrolysis of sucrose to form invert sugar, which is a mixture of dextrose and levulose. Lime is added to the juice, the mixture heated to boiling, and then allowed to settle. The clear juice is drawn off, and the sediment passed through the filter presses. The juice has to be evaporated down, the final stage in a vacuum. When it reaches the proper concentration, the sugar crystallizes out or "grains" and is separated by centrifuging. This method results in raw sugar which contains about 95 to 98 per cent of sucrose and a small amount of residual mother-liquor. Raw sugar is sold on its polarization value, that is, its sucrose content. Sometimes raw sugar is high enough in sucrose to be used without any further treatment, where the color is not objectionable.

In the manufacture of beet sugar the beets are cleaned, shredded and extracted with warm water in a series of extraction cylinders. The product, called diffusion juice, is purified by the following double carbonation process. Quick-lime or lime-cream and carbon dioxide gas are added to the juice. After the calcium carbonate settles, the juice is pumped through filter presses. The clear filtered juice is still alkaline and is treated with carbon dioxide again until the alkalinity is reduced to 0.03 or 0.06 per cent of lime, which causes further precipitation of calcium carbonate and necessitates a second filtration. The resulting liquid is transparent and light colored. In some factories this is further bleached with sulfur dioxide gas and filtered. The liquid is evaporated, the sucrose crystallized out and separated, as in cane-sugar manufacture.

Molasses is the mother liquor left after the sugar crystals have been separated. It has a high content of sucrose, as well as of invert sugar, and mineral and organic impurities derived from the original juice. Sometimes this molasses is reboiled to separate another crop of crystals, but the tendency is to recover the maximum amount of "first sugar" and to sell the "first molasses," which finds use in confectionery and bakery products because of its flavor. Poorer grades are used in cattle-food and in the production of alcohol. Blackstrap and New Orleans grades of molasses are widely sold.

Ordinarily the bagasse or crushed and extracted cane provides all the fuel necessary for steam production in the sugar mill. It is also used as a source of cellulose. The filter-press cakes from cane sugar contain lime and nitrogen, as well as other mineral and organic matter, and are used as fertilizer. The beet-pulp left after extraction of the juice is used as fodder. The filter-press cakes from beet sugar are sometimes used as fodder but are more apt to be discarded.

Washed sugar or **plantation sugar** is the next stage in purification. Raw sugar is frequently shipped to refineries near the point of use. It is washed to remove color and other impurities by spraying the layer of sugar in the centrifugal drum with a mixture of sirup from a later stage and water, while rotating at full speed. Ultramarine and water are used in the same way to blue the sugar. Such sugar is evaluated by its sucrose content and color, and can be used wherever refined sugar is used, provided it is sufficiently pure and free from color.

Refined sugar or **granulated sugar** is a recrystallized grade. Raw sugar is washed, then dissolved in water, run through bone-black or vegetable carbon filters to remove color and some phosphates, after which the liquid is again evaporated and recrystallized. The dried crystals are sieved and classified according to size as standard, medium and manufacturers' fine, the last being the most used as table sugar. Cube or loaf sugar may be molded directly from the refined sugar but it is also crystallized in slabs as **caster sugar** and cut up by saws.

Pulverized sugar is prepared for use in icings and in some types of confectionery by grinding granulated or caster sugar to a fine powder. There are different grades, known as fruit powdered, confectioners, powdered XXXX, and sometimes a special XXXXX sugar is offered. That known as confectioners' sugar normally has a small amount of starch added to reduce the tendency to cake.

Refiners' sirup, sugarhouse molasses or **treacle** is the sirup which remains after the sugar is separated from the refined and decolorized liquid. Its flavor is not due to compounds occurring naturally, but to the breakdown of sugars during the process of reboiling. It is somewhat of the type of caramel in taste and character and is used as a blending agent for flavoring.

Soft sugar is produced from refiners' sirup. As this sirup is boiled down, the sugar separating out takes on more and more color. The sirup from the first separation of refined sugar may be boiled down to separate a soft white sugar. The liquid left from this may be boiled down in turn, to give a somewhat darker sugar. In this way soft whites, soft yellows, and soft brown sugars are produced. The reason for the change in properties is a concentration of mineral matter, and an increase in invert sugar and moisture content. The medium brown has a delicious flavor, but the dark brown becomes less pleasant in taste. These sugars are used extensively in bakery products and in a fluffy type of confection.

Maple sugar is essentially sucrose but possesses a distinctive and very pleasing flavor due to the presence of impurities associated with the sugar in the sap of the maple tree. It is largely used as a flavor. There are legal restrictions on the application of artificial maple flavors.

Maltose, $C_{12}H_{22}O_{11}$, does not occur as a natural sugar but is produced by the hydrolysis of starch. It is a disaccharide which hydrolyzes to dextrose. Maltose itself is of little commercial importance. It is a fermentable sugar and plays a part in brewing.

Lactose or **milk sugar**, $C_{12}H_{22}O_{11}$, is a disaccharide occurring in milk. It yields dextrose and galactose on hydrolysis. Lactose is recovered from the whey from cheese manufacture. It is less sweet and less soluble than sucrose and is considered more beneficial as a food. There is a U.S.P. grade containing not more than 0.1 per cent of ash. This sugar is used in infants' food, in medicine and in confectionery.

Invert sugar is produced by the hydrolysis of sucrose and is composed of chemically equivalent parts of dextrose and levulose. It is not sold in dry form as it takes up water too readily, but it can be obtained as a sirup. Its property of absorbing and holding water makes it useful in products where loss of moisture is to be avoided.

Dextrose is also called by the more general names of **glucose** and **grape sugar.** It is a product made chiefly by the hydrolysis of starch. It is a hexose, $C_6H_{12}O_6$, which usually crystallizes with one molecule of water. It is sold as the monohydrate, which gives it a content of about 10 per cent of moisture, in the anhydrous state, and as a liquid U.S.P. product containing not more than 0.5 per cent of ash. A commercial form is **corn sugar** from the hydrolysis of corn starch. It is used in confectionery to give special consistencies, in baking, in brewing, in tanning as a filling agent, in many chemical operations as a reducing agent, in medicine, and for the production of caramel or sugar coloring. **Honey** is a solution of dextrose collected by bees from the nectar of flowers, having a characteristic flavor according to the flowers from which it is derived.

Corn sirup is sometimes called glucose by the confectionery trade, but chemically it is usually a mixture of dextrins, maltose and dextrose. Corn starch is hydrolyzed partially or wholly into dextrose, the amount of change determining the consistency of the finished sirup. It is sold on its solids content, and is spoken of by its Baumé reading of 42°, 43°, etc. Corn sirup is produced in large quantities, and is used as a food, for its bodying effect, in baked goods, etc. It has a pleasant and characteristic taste. Some pediatricians recommend it for use in infants' formulas.

Levulose is a hexose, $C_6H_{12}O_6$, also called fructose, produced by the acid hydrolysis of inulin from the Jerusalem artichoke. It has not been available to any great extent in the past, but is becoming more so. Levulose is used is a sweetening agent by diabetics.

Mannitol while closely related to the sugars, is an alcohol and described in that chapter.

CHAPTER XXXVII

PROTEINS

The usual conception of proteins is that they are a type of food, such as lean meat, but that does not tell the whole story. **Proteins** are highly complex substances sold in a variety of forms ranging from edible gelatin to nitrogenous by-products for fertilizers. They are present in all living matter, the basis of that fundamental life substance called protoplasm. Plants are able to build up these complex substances from very simple starting materials such as nitrates or ammonium salts taken up from the soil. The animal organism must obtain its protein material from plants or from the flesh of other animals.

Proteins vary in composition, but all contain carbon, hydrogen, oxygen and nitrogen. The presence of nitrogen is one differentiation from carbohydrates. Many contain sulfur and some contain phosphorus. The average composition might be expressed as carbon 51, oxygen 25, nitrogen 16, hydrogen 7, sulfur 0.4, and phosphorus 0.4 per cent. Molecular weight determinations for such complex substances are not very satisfactory, but minimal molecular weights are of the order of 5,000 to 30,000 with probable molecular weights of 30,000 to 200,000.

Proteins are hydrolyzed or broken down by heating in water, as well as by the action of the enzymes pepsin, trypsin and erepsin. Partial hydrolysis produced by the action of water converts proteins into proteoses, peptones and amino acids. The amino acids are the building blocks of proteins. These contain at least one carboxylic group and one amino group. The amino acids are united by a condensation between the carboxylic group of one compound and the amino group of another, with the loss of a molecule of water. This sort of union is called a peptide linkage and where two amino acids are joined in this way, the products is called a dipeptide.

Amino acids may be quite simple in structure, for example **glycine,** CH_2NH_2COOH, **aminoacetic acid.**

Because proteins contain both basic and acidic groups, they are amphoteric in nature. Each protein has an isoelectric zone, which can be expressed as a limited pH range where the acidic and basic dissociations balance one another. In solutions more acid than this, the protein behaves like a base, in solutions more alkaline, it behaves like an acid. For example, the isoelectric zone, more commonly called the isoelectric point, of gelatin, is about pH 4.7. Below this, the amino groups react, above this, the carboxyl groups.

The size of the protein molecule or molecular aggregate is such that in water it is neither in true solution nor in physical suspension, but in a state termed colloidal. This represents a border region between solution and suspension and is associated with a particle of size of about 1 to $100\mu\mu$ or millimicrons; 1×10^{-7} cm. or 1×10^{-6} mm. equals $1\mu\mu$. Colloidal solutions or suspensions possess properties which partake somewhat of the nature of true solutions and somewhat of the nature of suspensions of discreet particles. No sharp line can be drawn, sometimes they tend more toward the former condition and sometimes more toward the latter.

Gelatin is offered in commerce in varying degrees of purity. That prepared from fresh, clean stock under sanitary conditions is called gelatin, as distinguished from the less pure forms which constitute **glue.** Gelatin and glue are obtained from animal matter—bones, skin and tendons, principally from beef and calves. The material common to these parts of the animal is a protein called collagen.

The stock is first soaked, bones in hydrochloric acid and skins in lime water, to remove undesirable constituents and promote subsequent hydrolysis. The soaked and washed stock is then heated in water to about 70° C. to hydrolyze the collagen to gelatin. The temperature has to be controlled to prevent further hydrolysis of gelatin. After some hours, the first liquor is drawn off to give the best grade of gelatin. More water is added to the stock and several runs are made in this way, the last producing an inferior grade of glue. The solutions are clarified, concentrated in vacuum pans, chilled, and dried in warm air. The product is hard and is sold in sheets, flakes, shreds or pulverized as a coarse or fine powder. The sheets usually bear indentations of a coarse mesh screen on which they have been dried. Grades from edible gelatin to the lowest grades of glue tend each to merge into the next lower grade, so far as uses are concerned.

Edible gelatin is a transparent, nearly colorless substance which swells to many times its normal volume in water. There is a U.S.P. standard which defines it as the product of partial hydrolysis of collagen derived from the skin, white connective tissue and bones of animals.[1] Swollen gelatin, heated to 35° C., goes into solution. If such a solution contains more than 1 per cent of gelatin it sets to a solid gel when cold. It is also soluble in glacial acetic acid or aqueous glycerine but insoluble in the other organic solvents. Gelatin is used as a food in various ways. It appears as jellied desserts, salads, jellied consommé, jellied meats, in puddings and other forms. In some of these the natural gelatin of a food product has been extracted and concentrated. It is used extensively in the manufacture of ice cream, as it gives body and serves as a protective colloid, and tends to prevent crystallization or graininess in the product. Gelatin finds use in many confectionery and bakery products, such as marshmallows, icings, emulsion flavors, meringues, etc. It is formed into capsules for medicinals, and is used as a culture medium. Gelatin is a bodying agent for many technical products, a sizing material for expensive forms of papers, and in special inks. For many of these purposes edible gelatin is used for its physical rather than chemical properties. It reacts with bichromate to give a true tanned protein when exposed to light and this is the basis of a whole group of reactions.

Isinglass is a high grade of gelatin produced from the air bladders of certain fish, largely sturgeon. The sounds or bladders are cleaned and need no other preparation but drying.

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[1] The Food and Drug Administration requires that the edible grade contain less than 0.018 grain of lead and less than 0.01 grain of arsenic calculated as arsenious oxide and less than 0.01 grain of fluoride, per pound.

Various descriptive names are applied, according to whether the original bladder is unopened, opened or folded. These include "purse" or "lump," "leaf" or "honeycomb," "book," and "ribbon" isinglass. The principal use of isinglass is for clarifying wines, beers, vinegars, etc. For most of its uses, gelatin should serve. Also isinglass can replace gelatin in many of its applications but is in general more expensive.

Patent isinglass is a very pure form of gelatin lacking the structure of isinglass. It is used in making jellies and jams. Mixed with gum it gives a fine luster to silk, It is incorporated in India ink. Dissolved in two parts of alcohol, it forms a diamond cement; dissolved in strong acetic acid it forms a cement suitable for repairing glass and pottery.

Technical gelatin as well as glue, is sold primarily on the basis of the firmness of the jelly produced in solutions of specified concentration. Gelatin and glue merge into one another. Technical gelatin is used extensively in photography and photolithography. Its function is primarily that of a protective colloid. It retards the rate of aggregation of the reduced silver atoms on the photographic plate, and also acts as a mechanical binder. Scientists use it as a culture medium, and in the preparation of ultrafiltration cells. It is used as a protective colloid in electrometallurgical and other processes.

Hide glue or **skin glue** is made from the parings and cuttings of hides from tan yards, ears of oxen and sheep, and skins of smaller animals. There are many grades of hide glue according to the quality of raw materials from which it is made, the degree of hydrolysis which it has undergone in preparation, and other factors. Some are quoted according to the type of skin, such as **rabbit glue.** Hide glues are quoted on the highly technical basis of the viscosity of a 12.5 per cent solution at 60° C. in millipoises, over jelly strength in grams to produce a 4-mm. depression in the cold glue with the Bloom Gelometer—grades varying from 53/135 to 125/379 with a price variation approaching 50 per cent from the lowest to the highest grade. Occasionally glue is quoted by color for special uses.

Glue finds many uses as an adhesive and a sizing agent. It is an important adjunct in the wood-joining and veneer trades. Other applications are in making paper boxes, as a leather adhesive, for water-proofing fabrics, as a size for wall paper and coated papers. Glue is used as a size in the dyeing of fabrics and in finishing processes. Carpets and burlap wall coverings are sized with glue. Barrels to be used for non-aqueous liquids are lined with it. It serves as a size for the treatment of walls before painting, and may be mixed with a little paint, an insoluble base, and water in the preparation of **calcimine.** As a binding agent, it is used in composition cork, imitation hard rubber, matches and other items. As adhesives, these glues are applied warm, but should not be kept at high temperatures over a long period, as this results in loss of adhesive properties.

Since many adhesives are called glues, although in no way related to the protein substance glue, the duplication of words is sometimes confusing. Dextrin solutions are often called glues or sometimes more specifically vegetable glues. Therefore not all glues fall in this chemical classification.

Bone glue is made from the collagen in bones, after getting rid of fat and mineral matter. It is a substitute for hide glue in some of the applications where a high degree of technical quality is not essential. It is similarly quoted but is substantially lower in price and quality.

Fish glue is prepared from the waste products from the fish industries, and is the most important glue in the liquid state. The skins from the cod and cusk make a superior grade of glue. It is used for the making of half-tone plates for photo-engraving work. These glues give a flexible adhesive, suitable for bookbinding and for the backs of stamps and labels. The poorer grades are used for general adhesive purposes, as in the manufacture of paper boxes.

Furniture glue or **carpenters' glue** is a high-grade product necessarily applied hot because it is solid at room temperature. **Prepared glue,** when it is glue rather than other form of adhesive, is usually low-grade fish glue.

Albumin is another general type of protein found in many animal and vegetable sources, as in egg, muscle, milk, blood, and vegetable tissues and fluids. Albumins usually occur as a mixture rather than as a single individual substance. They swell in water and gradually dissolve.

Egg albumin is white of egg separated from the egg yolk and sold both in the liquid and the dried state. Domestic edible grades are substantially more expensive than imported. Outside of the bakery industry, one important main use for this material is as a clarifying agent. Egg albumin has the property of coagulating when heated and carrying down coloring matter and other impurities in the process. Sparkling clear gelatin solutions are obtained by filtering the solution and then clarifying with egg albumin. Albumin is similarly used in sugar refining. Other uses are in sizings, leather finishing, adhesives, printing textiles, etc.

Blood albumin is obtained from the blood of slaughtered animals by coagulating the corpuscles and the fibrin, and evaporating the clear serum under reduced pressure. The temperature must not exceed about 70° C. or the albumin will coagulate. The dried material is ground and sold as blood or serum albumin. Grades are dark flake, dark powdered, light flake and light powdered. Some imported grades are offered. Blood albumin is used in the manufacture of water-resistant glue. Vegetable glues are rather poor in this respect. The albumin must be reasonably fresh, as it becomes less soluble on aging. Ammonium hydroxide and lime are added to water and the albumin dissolved in this. The adhesive is applied to a joint and the latter placed in a hot press to effect coagulation and hardening. This adhesive is more water-resistant than that made from casein. Other uses parallel those of egg albumin.

Casein is the term applied to a group of related products which, like albumins, have the same general reactions. It occurs in milk from all sources and is separated from cow's milk on a commercial scale. In milk it exists as calcium caseinate in colloidal suspension. Casein is soluble in dilute alkalies and concentrated acids, but is precipitated in weakly acid solutions. It swells but does not dissolve to any great extent in water. Its concentration in milk is about 3 per cent, and in skim milk from which cream or butter has been separated, from 3 to 3.25 per cent. On long standing in contact with water it hydrolyzes to amino acids. Unless preserved it will spoil in water due to putrefaction.

Acid casein is the most common grade produced from skim milk, of which vast quantities are available due to the demand for butter and cream. Either sulfuric or hydrochloric acid is used in very dilute solution to coagulate the casein. The product is often designated by the acid used for precipitation. The curd is separated, washed, dried and ground. The color of the amorphous solid ranges from straw to buff, according to the degree of control of the manufacturing process and the resultant purity. Some acid is always retained by occlusion. Acid casein is soluble in dilute alkali and reprecipitated by dilute acid. General commercial grades are domestic, unground, ground to pass 20-30 mesh, and ground to pass 80-100 mesh. There are similar Argentine grades. Some French casein is also available.

Casein has many commercial uses. It is mixed with lime and other alkaline agents to make a glue or cement which is much more water-resistant than animal glues. It may be prepared with water in a few minutes' time. It forms a jelly on standing and should be used within a few hours. It is frequently called "cold-water glue" because, unlike animal glues, it is mixed with cold water and applied cold.

Casein serves as a binder in many cold-water paints. It increases the water resistance of such paints, sufficiently so that the painted surface can be washed with water, a use usually limited to interior work. Mixtures of this type are also used as water colors in the printing of wall papers and for the printing of patterns on certain kinds of fabrics such as calico.

Casein is used as a binder for pigments in coating paper. Paper coated with casein takes ink very sharply, so that designs are accurately reproduced. The casein solution contains borax and a small amount of ammonia, which increases water-resistance. The chief difficulty is to get a solution of the proper viscosity.

A lime-casein mixture is applied as a sizing coat to the interior of barrels to be used as oil containers. This type of size is also applied to plastered walls before painting. Casein is often an ingredient of massage creams, ointments, and cosmetics. When the cream is rubbed over the skin, the casein forms rolls which pick up the dirt and are themselves readily removed.

In many instances a lime-casein mixture is used for the same purposes as animal glue, and is therefore more or less interchangeable with the latter. Acid casein is used to some extent in the plastics industry, but not nearly as much as rennet casein, as the former gives more brittle and less uniformly colored products.

Self-soured casein is produced by lactic acid formation. The skim milk is treated with a little sour milk or culture of lactic acid bacteria to start the curdling process. The curd is separated and treated much the same as in the acid method of preparation. The purity of the product depends on temperature control, the extent of washing, etc. In general, self-soured casein resembles acid casein in appearance and properties and is applied to the same commercial uses. When very pure, this form may be used as a food.

Rennet casein is produced by enzyme action. Rennet is an enzyme which causes the precipitation of casein from sweet milk, the method thus differing from the two previous methods of coagulation. Fresh skim milk from which the butter fat has been separated as completely as possible, is used. The curd is separated, washed and dried. A high-quality product is produced, having a color varying from cream to white. The fat content is usually lower than in other caseins. The precipitated casein appears to be in its original form and is therefore designated by some as **calcium caseinate.** Another name given it is **paracasein.** Rennet casein is somewhat less soluble in alkalies than acid casein. The viscosity of the solution tends to be greatest with the rennet casein and least with self-soured casein. It is precipitated from alkaline solution by acids.

Rennet casein is largely used in the manufacture of **casein plastics.** Such material is hard, takes a high polish, and can be dyed and tooled. Like other plastics, it is used in making umbrella handles, novelties, beads, automatic pencils, etc. In one process the casein is put into solution, mixed with pigments and sometimes fillers, coagulated, pressed into the desired shape, hardened with formaldehyde and seasoned. In the more generally used process, the ground casein is kneaded with the other ingredients in the presence of water, pressed, hardened with formaldehyde and dried.

Rennet casein is used in making confectionery and in special foods. Dissolved in a solution of sodium bicarbonate or sodium glycolate or lactate, it is very readily digested. Preparations are also used as media for the medicinal administration of drugs such as quinine.

Wool substitutes are produced from casein by methods analogous in principle to preparation of rayon, using aldehydes as setting agents. While not yet commercially available their further development may reasonably be expected.

Soybean proteins are the ground soybeans from which the oil has been pressed. The material has about 50 per cent protein content, and is sold in ground form for plastic manufacture.

Milk powder is a food product high in protein, prepared by evaporating whole or skimmed milk to dryness. Two processes are in common use, spraying into an ascending column of hot air and flowing on a hot roll from which it is removed by a scraper. The powder contains the solids and fat of the grade of milk used and about 5 per cent of residual moisture. Grades sold are skimmed and unskimmed, both roller- and spray-dried. It is used as a food, as in baked goods, proprietary mixes, infants' food, animal foods, etc.

Linseed meal is ground linseed or flaxseed, the dried ripe seeds of *Linum usitatissimum,* which has not been pressed. It is sold to contain 32 per cent of oil. There is a grade for medical use, largely as poultices. The tonnage market is as a high-fat food for animals and for pressing out linseed oil.[1] **Cottonseed meal** and other seed meals are similar in derivation and use.

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[1] The linseed from which the meal is produced is a U.S.P. product containing not more than 2 per cent of other seeds or foreign organic matter and containing not less than 30 per cent of ether-extractable oil of which at least 98 per cent is saponifiable.

Linseed cake is the residue remaining after ground linseed has been subjected to hydraulic pressure to press out the oil. It contains all of the protein of the seed with a minimum of oil. It is used as a cattle food, as fertilizer and for other purposes where a by-product protein is needed. **Cottonseed cake** and other cakes from oil-bearing seeds are similar in composition and use.

Dried blood is a red to brown, solid, amorphous by-product from the meat-packing industry. The blood is coagulated, dried and powdered and then contains somewhat over 1 per cent of phosphorus. It is only partially soluble in water. Grades sold are domestic containing 16-16.5 per cent ammonia, high-grade ground, with 16-17 per cent ammonia content, and imported. It is used as a nitrogenous ingredient in fertilizers, as a clarifying agent for liquids such as sugar solutions because of its protein content, in patent medicines, in adhesives, for feeding animals and fowls and as a vehicle for special paints.

Castor pomace is the residue left after the oil has been extracted from the castor bean. A domestic grade is sold to contain 5.5 per cent of ammonia. Usually 1-1.5 per cent of phosphoric acid and an equal amount of potash are present. It is used as an ingredient of mixed fertilizers.

Animal tankage consists of the by-product residues from slaughter houses. After the recovery of fat and gelatin, the material is dried with the addition of 15-20 per cent of by-product lime, unless intended for feeding. Processes are complex and often include use of evaporated tank waters. For fertilizer use, a domestic grade of animal tankage is sold to contain 10-12 per cent of ammonia, and unground at 9-11 per cent of ammonia, both with 15-20 per cent of lime. An imported 10-12 per cent ammonia, 15 per cent by-product lime-grade is also sold. Tankage can be used for animal feeding and a high grade, of feeding type, is quoted. Railroad regulations require the presence of at least 8 per cent of moisture. Quotations are on a basis of the ammonia content in dollars per unit.

Fish scrap is the residue left from fish carcasses after they have been cooked and the oil expressed. **Dried fish scrap** is the dried residue sold as gound and unground, to contain 11-12 per cent of ammonia and 15 per cent of bone phosphate. The moisture content is usually over 8 per cent. **Wet fish scrap** is prepared by mixing the wet residues with sulfuric acid to retain ammonia and solubilize phosphates. It is sold to contain 6-7 per cent of ammonia and 3 per cent of phosphoric acid. The water content often exceeds 50 per cent. The market for fish scrap is as fertilizer. Quotations often mention the source, such as **menhaden scrap. Sardine meal** is a form of dried fish scrap prepared under such conditions that it is suitable for poultry and animal feeding. It is sold on an 11.5 per cent nitrogen basis. The usual source is an imported Japanese grade.

Garbage tankage is the residue left after treatment of garbage to recover fat. It contains a few per cent of ammonia nitrogen, of phosphates, and a fraction of a per cent of potash. It is a low-grade fertilizer which as ordinarily produced, will not have sufficient values to justify shipment for any considerable distance.

Nitrogenous fertilizer material is a class of material of diverse organic origin, used in mixed fertilizers as a source of available nitrogen for plants. It is sold to contain 8-11 per cent ammonia, imported and domestic. Prices are based on the available nitrogen or "unit-ton" of 1 per cent available nitrogen. Chemical nitrogenous products are competitive with the organic by-product materials.

Fertilizers as a general term means mixed fertilizers containing potash, nitrogen and phosphorus in substantial quantities, sold by analysis as legally required.

APPENDIX A

U. S. CAUSTIC POISON ACT

This act applies to all sales in interstate commerce, and classifies as a dangerous caustic or corrosive substance the following:

1. Free hydrochloric acid over 10 per cent.
2. Free sulfuric acid over 10 per cent. This includes the equivalent in sodium bisulfate or other acid salts.
3. Free nitric acid over 5 per cent.
4. Phenol, carbolic acid, over 5 per cent.
5. Free oxalic acid over 10 per cent.
6. Salts of oxalic acid over 10 per cent.
7. Free acetic acid over 20 per cent.
8. Free or combined hypochlorous acid in an amount equivalent to over 10 per cent of free chlorine. Free hypochlorous acid is unstable so this means in practice liquid chlorine bleaches. The provision does not apply to chloride of lime, bleaching powder.
9. Free potassium hydroxide over 10 per cent.
10. Free sodium hydroxide over 10 per cent.
11. Silver nitrate over 5 per cent.
12. Free ammonia over 5 per cent, including that present in aqueous solution, such as aqua ammonia.

When any of these caustic poisons are present the product must be branded with the following:

1. The common name of the substance.
2. The name and place of business of the manufacturer, packer or distributor.
3. The word "poison" running parallel with the main body of reading matter on the label or sticker, on a clear, plain background of a distinctly contrasting color, in uncondensed gothic capital letters, the letters to be not less than twenty-four point size unless there is on the label or sticker no other type so

large, in which the event the type shall be not smaller than the largest type on the label or sticker.

4. Directions for treatment in case of accidental personal injury by any dangerous caustic or corrosive substance, what is usually known as the "antidote," except that such directions need not appear on labels or stickers, on parcels, packages or containers at the time of shipment or of delivery for shipment by manufacturers and wholesalers for other than household use.

Copies of the act and recommended forms of antidote can be obtained from offices of the Food and Drug Administration of the Department of Agriculture.

The above summary is intended only to indicate the substances covered and the details of compliance with proper labeling regulations.

APPENDIX B

The following are brief, free translations of medical terms used.

Abortifacient, produces abortions; **alterative,** changes morbid state of health; **analgesic,** produces insensibility to pain; **anesthetic,** produces loss of feeling; **anodyne,** allays pain; **anthelmintic,** expels or destroys intestinal worms; **antiasthmatic,** relieves asthma; **anticatarrhal,** relieves catarrah; **antidiarrhetic,** prevents diarrhea; **antidysenteric,** relieves dysentery; **antihydrotic,** prevents release of water or phlegm; **antihysteric,** prevents or relieves hysteria; **antilythic,** prevents or destroys urinary calculi; **antineuralgic,** relieves neuralgia; **antiparasitic,** kills parasites; **antiperiodic,** prevents returns of paroxysms, as in intermittent fever; **antipodagric,** relieves gout; **antipruretic,** relieves itching; **antipyretic,** relieves fever; **antirheumatic,** relieves rheumatic pains; **antiscorbutic,** counteracts scurvy; **antiscrofular,** counteracts the morbid condition of scrofula; **antiseptic,** kills microorganisms; **antisialagogue,** arrests flow of saliva; **antispasmodic,** sedative to nervous system; **antisyphylitic,** a remedy or sometimes a relief for syphylis; **antitetanic,** relieves tetanic spasms; **aperient,** a gentle laxative; **aphrodisiac,** excites sexual organs; **aromatic,** having a pungent odor and usually a warm pungent flavor; **astringent,** contracting the tissues; **carminative,** relieves colic by expelling gas from gastric canal; **cholagogue,** promotes discharge of bile from the system; **corrigant,** counteracts disagreeable effect of the main ingredient of a medicine; **counterirritant,** produces an irritation or even a blister to relieve discomfort elsewhere; **demulcent,** soothing to inflamed or irritated mucous membrane; **depressant,** lowers functional activity; **diaphoretic,** increases perspiration; **digestive,** aids digestion; **diuretic,** increases secretion of urine; **emetic,** induces vomiting; **emmenagogue,** promotes menstrual discharge; **emollient,** a soothing or softening agent; **errhina,** causes sneezing; **excitomotor,** stimulates motor nerve centers; **expectorant,** promotes discharge of mucus; **febrifuge,** relieves or removes fever; **galactagogue,** promotes secretion of milk; **hemostatic,** arrests hemorrhage; **hydragogue,** expels serum, usually a diuretic or cathartic; **hypnotic,** produces sleep; **irritant,** produces inflammation; **local irritant,** produces localized irritation; **masticatory,** chewed to promote salivation; **mydriatic,** dilates the pupil of the eye; **myotic,** contracts the pupil of the eye; **narcotic,** allays pain and produces sleep but in excessive amounts produces coma and convulsions; **nephritic,** relieves inflammation of the kidneys; **nervine**, soothes nervous excitement; **oxytocia,** hastens childbirth; **parturient**, assists childbirth; **pectoral**, relieves diseases of the chest or lungs; **purgative,** strongly cathartic; **refrigerant,** allays fever; **resolvent,** causes solution; **rheumatic,** tends to cause watery discharge from eyes, nose and throat; **rubefacient**, produces reddening of the skin; **sedative**, allays irritability, nervous excitement and pain; **sialagogue,** promotes flow of saliva; **spinant,** increases reflex excitability of the spinal cord; **sternutic,** causes sneezing; **stimulant,** produces temporary increase of vital activity; **stomachic,** has tonic effect on stomach; **sudorific,** induces perspiration; **tenafuge,** expels tapeworms; **vermifuge,** expels or destroys intestinal worms; **vesicant,** produces blisters; **vulneric,** promotes healing of wounds.

APPENDIX C

Summary of the Food, Drug and Cosmetic Act. Effective June 25, 1939, except items 13, 14 and the prohibitions of item 1, which were effective June 25, 1938.

1. Controls all cosmetics except toilet soap, forbids those which may be injurious to users, except coal-tar hair dyes which must bear warning labels, and prohibits false or misleading labeling.

2. Prohibits traffic in food which may be injurious to health.

3. Prohibits addition of poisonous substances to food except where such addition is required in production of the food, or cannot be avoided by good manufacturing practice, and in the latter cases, establishes tolerances to an amount insuring protection of public health.

4. Authorizes emergency permits to control food which may be injurious because of contamination with microorganisms, unless public health can be otherwise protected.

5. Forbids traffic in confectionery containing metallic trinkets and other inedible substances.

6. Requires declaration on the label of artificial coloring, artificial flavoring and chemical preservatives in food, except artificial color in butter, cheese and ice cream.

7. Requires declaration on the label of special dietary foods of vitamin, mineral and other dietary properties.

8. Provides for promulgation of a definition and standard of identity, and a reasonable standard of quality and fill of container for each food, except fresh and dried fruits and vegetables, avocados, cantaloupes, citrus fruits and melons. Butter is excepted but the old definition of standard and identity is retained.

9. Requires the labeling of food for which no definition and standard of identity has been fixed, to disclose the ingredients by name, except spices, coloring, and flavoring, which may be described as spices, coloring, and flavoring. Authorizes

exemptions where compliance is either impractical or results in deception or unfair competition.

10. Avoids the "distinctive name" clause under which any mixture or compound of food not injurious to health can escape control.

11. Brings under control all drugs used in the diagnosis of disease and drugs intended to affect the structure or any function of the body.

12. Subjects therapeutic devices to the same general requirements as drugs.

13. Prohibits sale of drugs and devices dangerous to health under the conditions of use prescribed on the label.

14. Prohibits sale of new drugs until adequately tested to show that they are safe under the conditions prescribed on the label, except for investigational use by qualified scientific experts.

15. Makes the Homeopathic Pharmacopoeia of the United States the legal standard for homeopathic drugs.

16. Requires labels of official drugs recognized by inclusion in the United States Pharmacopoeia, National Formulary or Homeopathic Pharmacopoeia of the United States to show any differences of strength, quality or purity from the official standard.

17. Requires labels of drugs intended for use by man, to warn against any habit-forming substances such as narcotics, hypnotics, or their derivatives having similar properties. The specified substances are *alpha*-**eucaine, barbituric acid,** *beta*-**eucaine, bromal, cannabis, carbromal, chloral, coca, cocaine, codeine, heroin, marihuana, morphine, opium, paraldehyde, peyote, sulfonmethane.** Additions may be made to the list.

18. Requires that labels of drugs and devices bear adequate directions for use but authorizes exemptions where not necessary for protection of public health.

19. Requires that labels of drugs and devices bear warnings against probable misuse which may be dangerous to health.

20. Requires special precautionary labeling for drugs liable to deterioration.

21. Does not require that the Government prove that false claims of curative effect on patent medicines were made with willful intent to deceive.

22. Requires that official drugs be packaged and labeled as prescribed by the Pharmacopoeias and Formulary.

23. Declares nonofficial drugs illegal if the standard of strength differs from the standard claimed.

24. Requires that antiseptics possess germicidal power.

25. Requires that labels of nonofficial drugs list the names of the active ingredients and the quantity of the following substances: **alcohols, bromides, ether, chloroform, acetanilide, acetphenetidin, amidopyrine, antipyrine, atropine, hyoscine, hyoscyamine, arsenic, digitalis, digitalis glucosides, mercury, ouabain, strophanthin, strychnine, thyroid,** and any derivative of such substances. Exemptions are authorized where compliance is impracticable.

26. Forbids the use of containers for food, drugs and cosmetics which may render the contents injurious to health.

27. Prohibits sale of food, drugs and cosmetics which have been prepared or handled under unsanitary conditions, which may contaminate them or render them injurious to health.

28. Forbids the use of uncertified coal-tar dyes in food, drugs and cosmetics other than in hair dyes.

29. Forbids slack filling of containers for food, drugs and cosmetics, and the use of deceptive containers.

30. Authorizes factory inspection of establishments producing food, drugs, devices, and cosmetics for interstate shipment.

31. Provides the means of procuring transportation records and other documents necessary to establish Federal jurisdiction.

32. Requires that parts of samples collected by the Government for analysis be given to the manufacturer on request, but provides exemption when impractical.

33. Authorizes charging of fees for certification of coal-tar dyes in amounts to pay the expense of the service.

34. Authorizes abatement of proceedings in case of minor violations when the public interest can be adequately served by a written notice or warning.

35. Increases the criminal penalties for violations.

36. Authorizes the Federal courts to issue injunctions against violations.

37. In case of misbranding, limits seizure to a single interstate shipment unless (1) a previous court decision has been in favor of the Government, (2) the article is dangerous to health, or (3) the label is fraudulent or materially misleading, and would result in injury or damage to the purchaser or consumer.

38. Authorizes consolidation of multiple seizures into a single case.

39. Authorizes trial of cases in a district agreed upon between the Government and the shipper or owner. By application to the court this can be made convenient to the defendant's place of business.

40. Provides for review in United States Circuit Courts of Appeals to determine the validity of some of the regulations, without limiting the present legal protection of defendants.

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